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MODIFIED CARBIDE AND OXYCARBIDE CONTAINING CATALYSTS AND METHODS OF MAKING AND USING THEREOF

RELATED APPLICATIONS

5   This application is a continuation-in-part of U.S. Application Serial No. 09/615,350 filed July 12, 2000 which is a continuation-in-part of U.S. Application Serial No. 09/481,184 filed January 12, 2000 based on U.S. Provisional Patent Application No. 60/115,735 filed January 12, 1999, which applications are hereby incorporated by reference in their entirety.

10

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to modified, e.g., acidified, compositions of carbide-containing and oxycarbide-containing nanorods, carbon nanotubes including carbide

15   and/or oxycarbide compounds, rigid porous structures including these compositions, and methods of making and using the same. More specifically, the invention relates to modified rigid three dimensional structures comprising carbide and/or oxycarbide-containing nanorods or carbon nanotubes bearing carbides and oxycarbides, having high surface areas and porosities, low bulk densities, substantially no micropores and

20   increased crush strengths. The invention also relates to using the modified compositions and the rigid porous structures including these compositions as catalysts and catalyst supports, in heterogeneous catalytic reactions frequently encountered in petrochemical and refining processes.

Description of the Related Art

25   Heterogeneous catalytic reactions are widely used in chemical processes in the petroleum, petrochemical and chemical industries. Such reactions are commonly performed with the reactant(s) and product(s) in the fluid phase and the catalyst in the solid phase. In heterogeneous catalytic reactions, the reaction occurs at the interface between the phases, i.e., the interface between the fluid phase of the reactant(s) and

product(s) and the solid phase of the supported catalyst. Hence, the properties of the surface of a heterogeneous supported catalyst are important factors in the effective use of the catalyst. Specifically, the surface area of the active catalyst, as supported, and the accessibility of that surface area to reactant adsorption and product desorption are

5   important. These factors affect the activity of the catalyst, i.e., the rate of conversion of reactants to products. The chemical purity of the catalyst and the catalyst support have an important effect on the selectivity of the catalyst, i.e., the degree to which the catalyst produces one product from among several products and the life of the catalyst.

       Generally catalytic activity is proportional to catalyst surface area. Therefore, a

10   high specific area is desirable. However, the surface area should be accessible to reactants and products as well as to heat flow. The chemisorption of a reactant by a catalyst surface is preceded by the diffusion of that reactant through the internal structure of the catalyst.

       Since the active catalyst compounds are often supported on the internal structure

15   of a support, the accessibility of the internal structure of a support material to reactant(s), product(s) and heat flow is important. Accessibility is measured by porosity and pore size distribution. Activated carbons and charcoals used as catalyst supports may have surface areas of about a thousand square meters per gram and porosities of less than 1 ml / gm. However, much of this surface area and porosity, as much as 50%, and often more,

20   is associated with micropores, i.e., pores with pore diameters of 2 nm or less. These pores can be inaccessible because of diffusion limitations. They are easily plugged and thereby deactivated. Thus, high porosity material where the pores are mainly in the mesopore region, i.e., greater than 2 nm or macropore region, i.e., greater than 50 nm, ranges are most desirable.

25   It is also important that self-supported catalysts and supported catalysts not fracture or attrit during use because such fragments may become entrained in the reaction stream and must then be separated from the reaction mixture. The cost of replacing attritted catalyst, the cost of separating it from the reaction mixture and the risk of contaminating the product are all burdens upon the process. In slurry phase, e.g. where

30   the solid supported catalyst is filtered from the process stream and recycled to the

reaction zone, the fines may plug the filters and disrupt the process. It is also important that a catalyst, at the very least, minimize its contribution to the chemical contamination of reactant(s) and product(s). In the case of a catalyst support, this is even more important since the support is a potential source of contamination both to the catalyst it

5 supports and to the chemical process. Further, some catalysts are particularly sensitive to contamination that can either promote unwanted competing reactions, i.e., affect its selectivity, or render the catalyst ineffective, i.e., "poison" it. For example, charcoal and commercial graphites or carbons made from petroleum residues usually contain trace amounts of sulfur or nitrogen as well as metals common to biological systems and may

10 be undesirable for that reason.

Traditionally, noble metal catalysts, such as platinum and ruthenium, have been used as catalysts in heterogeneous reactions. Because of the expense associated with the noble metal catalysts, many workers have sought to achieve a "poor man's platinum" through the use of metal carbides. To control the catalytic activity of metal carbides, 2

15 important factors need to be realized. First, the carbide particles need to have nanoscale dimensions in order to possess enough surface area. Second, the catalyst may need to undergo surface modifications to enhance the catalyst's ability to obtain special selectivity.

Since the 1970s carbon nanofibers or nanotubes have been identified as materials

20 of interest for use as catalysts and catalyst supports. Carbon nanotubes exist in a variety of forms and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces. Nanofibers such as fibrils, bucky tubes and nanotubes are distinguishable from continuous carbon fibers commercially available as reinforcement materials. In contrast to nanofibers, which have, desirably large, but

25 unavoidably finite aspect ratios, continuous carbon fibers have aspect ratios (L/D) of at least 10^4 and often 10^6 or more. The diameter of continuous fibers is also far larger than that of nanofibers, being always greater than 1 μm and typically 5μm to 7 μm.

U.S. Patent No. 5,576,466 to Ledoux et al. discloses a process for isomerizing straight chain hydrocarbons having at least 7 carbon atoms using catalysts which include

30 molybdenum compounds whose active surface consists of molybdenum carbide which is

partially oxidized to form one or more oxycarbides. Ledoux et al. disclose several ways of obtaining an oxycarbide phase on molybdenum carbide. These methods require the formation of molybdenum carbides by reacting gaseous compounds of molybdenum metal with charcoal at temperatures between 900°C and 1400°C. These are energy

5   intensive processes. Moreover, the resulting molybdenum carbides have many drawbacks similar to catalysts prepared with charcoal. For example, much of the surface area and porosity of the catalysts is associated with micropores and as such these catalysts are easily plugged and thereby deactivated.

While activated charcoals and other materials have been used as catalysts and

10   catalyst supports, none have heretofore had all of the requisite qualities of high surface area, porosity, pore size distribution, resistance to attrition and purity for the conduct of a variety of selected petrochemical and refining processes. Although many of these materials have high surface area, much of the surface area is in the form of inaccessible micropores.

15   It would therefore be desirable to provide a family of carbide-containing and oxycarbide containing catalysts that have highly accessible surface area, high porosity, and attrition resistance, and which are substantially micropore free, highly active, highly selective and are capable of extended use with no significant deactivation.

Objects of the Invention

20   It is an object of the present invention to provide a method of modifying the surface of a carbide-containing or oxycarbide-containing catalyst and/or a carbide-containing or oxycarbide-containing catalyst support to improve its properties.

It is a related object of the present invention to provide a method of modifying the surface of a carbide-containing or oxycarbide-containing catalyst and/or a carbide-

25   containing or oxycarbide-containing catalyst support to improve its selectivity.

It is a further object of the present invention to provide a method of modifying the surface of a carbide-containing or oxycarbide-containing catalyst and/or a carbide-containing or oxycarbide-containing catalyst support to improve its selectivity in hydrocarbon skeletal isomerizations.

It is another object of the present invention to provide such catalyst compositions and/or catalyst supports having modified surfaces.

It is yet a further object of the present invention to provide such catalyst compositions and/or catalyst supports having surfaces modified to improve reaction selectivity.

It is yet another and further object of the present invention to provide such catalyst compositions and/or a catalyst supports having surfaces modified to improve reaction selectivity in hydrocarbon skeletal isomerizations.

It is another object of the present invention to provide a composition of a catalyst and/or a catalyst support that has had its surface modified.

It is a further object of the present invention to provide a composition of a catalyst and/or a catalyst support that has had its surface modified to improve its selectivity.

The foregoing and other objects and advantages of the invention will be set forth in or will be apparent from the following description and drawings.

SUMMARY OF THE INVENTION

The present invention is in compositions comprising carbide nanorods which contain oxycarbides.. Another composition of the present invention comprises carbide-containing nanorods which also contain oxycarbides. Another composition comprises carbon nanotubes which bear acidified carbides and/or oxycarbides on the surfaces thereof. In one composition the carbides retain the structure of the original aggregates of carbon nanotubes. Compositions are also provided which include carbide-containing nanorods where the morphology of the aggregates of carbon nanotubes is not retained. The invention also provides a composition of carbides supported on carbon nanotubes where a portion of the carbon nanotubes have been converted to carbide-containing nanorods and/or carbides.

The present invention also provides rigid porous structures including acidified oxycarbide nanorods and/or carbide-containing nanorods and/or carbon nanotubes bearing carbides and oxycarbides. Depending on the morphology of the carbon nanotubes used as a source of carbon, the rigid porous structures can have a uniform or

non-uniform pore distribution. Extrudates of acidified oxycarbide nanorods and/or carbide-containing nanorods and/or carbon nanotubes bearing oxycarbides and/or carbides are also provided. The extrudates of the present invention are glued together to form a rigid porous structure.

5   The compositions and rigid porous structures of the invention can be used either as catalysts and/or catalyst supports in fluid phase catalytic chemical reactions.

The present invention also provides methods of making oxycarbide-containing nanorods, carbide-containing nanorods bearing oxycarbides and carbon-nanotubes bearing carbides and oxycarbides. Methods of making rigid porous structures are also

10   provided. Rigid porous structures of carbide-nanorods can be formed by treating rigid porous structures of carbon nanotubes with a Q-containing compound, i.e., a compound containing a transition metal, a rare earth or an actinide. Depending upon conditions the conversion of the carbon nanotubes to carbide-containing nanorods can be complete or partial. The rigid porous structure of carbide nanorods and/or carbon nanotubes can be

15   further treated with an oxidizing agent to form oxycarbide nanorods and/or oxycarbides. The rigid porous structures of the invention can also be prepared from loose nanorods or aggregates of carbide-containing nanorods and/or oxycarbide-containing nanorods by initially forming a suspension in a medium, separating the suspension from the medium, and pyrolyzing the suspension to form rigid porous structures. The present invention also

20   provides a process for making supported catalysts for selected fluid phase reactions.

Other improvements which the present invention provides over the prior art will be identified as a result of the following description which sets forth the preferred embodiments of the present invention. The description is not in any way intended to limit the scope of the present invention, but rather only to provide a working example of

25   the present preferred embodiments. The scope of the present invention will be pointed out in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of the specification, illustrate an exemplary embodiment of the present invention.

Figure 1A is an XRD graph of sample 12 as set forth in Table 1. A reference XRD pattern of hexagonal Mo_2C is shown immediately below.

Figures 1B and 1C are SEM micrographs of sample 12 as set forth in Table 1.

Figure 2A is an XRD graph of sample 12 as set forth in Table 1. A reference XRD pattern of hexagonal Mo_2C is also shown immediately below.

Figure 2B is an HRTEM micrograph of sample 12 as set forth in Table 1.

Figure 3A is an XRD graph of sample 10 as set forth in Table 1. Reference XRD patterns of hexagonal Mo_2C, cubic Mo_2C and graphite are shown immediately below.

Figure 3B is an HRTEM micrograph of sample 10 as shown in Table C.

Figure 4 is a thermogravimetric analysis of sample 12 as set forth in Table 1.

Figure 5A is an SEM micrograph of SiC extrudates.

Figure 5B is an SEM micrograph illustrating micropores among the aggregates of the extrudates shown in Figure 5A.

Figure 5C is an SEM micrograph illustrating micropores in the networks of the intertwined SiC nanorods present in the extrudates shown in Figure 5A.

DETAILED DESCRIPTION OF THE INVENTION

Patents, patent applications, and patent publications are referred to herein are incorporated by reference in their entirety.

Definitions

"Acidifying compound" means any compound capable of imparting an acidic characteristic to a catalyst and/or a catalyst support. Acidifying compound includes any compound that is capable of accepting electrons. "Accessible surface area" refers to that surface area not attributed to micropores.

"Aggregate" refers to a dense, microscopic particulate structure. More specifically, the term "assemblage" refers to structures having relatively or substantially uniform physical properties along at least one dimensional axis and desirably having relatively or substantially uniform physical properties in one or more planes within the

assemblage, i.e. they have isotropic physical properties in that plane. The assemblage

may comprise uniformly dispersed individual interconnected nanotubes or a mass of

connected aggregates of nanotubes. In other embodiments, the entire assemblage is

relatively or substantially isotropic with respect to one or more of its physical properties.

5   The physical properties which can be easily measured and by which uniformity or

isotropy are determined include resistivity and optical density.

"Bifunctional catalyst" means a catalyst that contains two distinct types of

catalytic sites in close proximity, for example on the same support, so that two chemical

reactions, for example sequential chemical reactions, can occur with one adsorption

10   event.

"Bimodal pore structure" refers to a specific pore structure occurring when

aggregate particles of nanotubes and/or nanorods are bonded together. The resulting

structure has a two-tiered architecture comprising a macrostructure of nanotube

aggregates having macropores among the bundles of nanotube aggregates and a

15   microstructure of intertwined nanotubes having a pore structure within each individual

bundle of aggregate particles.

"Carbides" refers to compounds of composition QC or Q_2C. The term also

includes crystalline structures characterized by x-ray diffraction ("XRD") as QC or Q_2C

by themselves and/or in combinations with Q or C, e.g., compounds remaining after the

20   synthesis step is substantially complete. Carbides can be detected and characterized by

XRD. When, as is contemplated within the scope of this invention, the carbides are

prepared by carburization of metal oxides or by oxidation of elemental carbon, a certain

amount of "non-stoichiometric" carbide may appear, but the diffraction pattern of the true

carbides will still be present. Metal rich non-stoichiometric carbides, such as might be

25   formed from a synthesis wherein the metal is carburized, are missing a few of the carbons

that the metal matrix can accommodate. Carbon rich non-stoichiometric carbides

comprise domains of stoichiometric carbides embedded in the original carbon structure.

Once the carbide crystallites are large enough they can be detected by XRD.

Carbides also refers to interstitial carbides as more specifically defined in

30   *Structural Inorganic Chemistry*, by A.F. Wells, 4th Ed., Clarendon Press, Oxford 1975

and in *The Chemistry of Transition Metal Carbides and Nitrides*, edited by S.T. Oyama, 1st Ed., a Blackie Academic & Professional publication 1996. Both books are hereby incorporated by reference in their entirety.

5 "Carbide-containing nanorod" refers to a Q-containing nanorod predominantly having a diameter greater than 2 nm but less than 100 nm, for example greater than 5 nm but less than 50 nm, and having an aspect ratio from 5 to 500. When the carbide nanorod has been made by conversion of the carbon of a nanotube to carbide compounds then the conversion has been substantially complete.

"Fluid phase reaction" refers to any liquid or gas phase catalytic reactions such as 10 hydrogenation, hydrodesulfurisation, hydrodenitrogenation, hydrodemetallisation, hydrodeoxygenation, protonation, hydrodearomatization, dehydrogenation, hydrogenolysis, isomerization, alkylation, dealkylation, and transalkylation.

"Graphenic" carbon is a form of carbon whose carbon atoms are each linked to three other carbon atoms in an essentially planar layer forming hexagonal fused rings. 15 The layers are platelets having only a few rings in their diameter or ribbons having many rings in their length but only a few rings in their width.

"Graphenic analogue" refers to a structure which is incorporated in a graphenic surface.

"Graphitic" carbon consists of layers which are essentially parallel to one another 20 and no more than 3.6 angstroms apart.

"Internal structure" refers to the internal structure of an assemblage including the relative orientation of the fibers, the diversity of and overall average of nanotube orientations, the proximity of the nanotubes to one another, the void space or pores created by the interstices and spaces between the fibers and size, shape, number and 25 orientation of the flow channels or paths formed by the connection of the void spaces and/or pores. According to another embodiment, the structure may also include characteristics relating to the size, spacing and orientation of aggregate particles that form the assemblage. The term "relative orientation" refers to the orientation of an individual nanotube or aggregate with respect to the others (i.e., aligned versus non-aligned). The

"diversity of" and "overall average" of nanotube or aggregate orientations refers to the range of nanotube orientations within the structure (alignment and orientation with respect to the external surface of the structure).

"Isotropic" means that all measurements of a physical property within a plane or volume of the structure, independent of the direction of the measurement, are of a constant value. It is understood that measurements of such non-solid compositions must be taken on a representative sample of the structure so that the average value of the void spaces is taken into account.

"Macropore" refers to a pore which has a diameter of greater than or equal to 50 nm.

"Mesopore" refers to a pore which has a diameter of greater than or equal to 2 nm but less than 50 nm.

"Micropore" refers to a pore which has a diameter of less than 2 nm.

"Nanorod" refers to a rod-like structure having a surface and a substantially solid core with a diameter of at least 1 nm but less than 100 nm. The structure has an aspect ratio between 10 and 500 and a length up to 50 μm. The diameter of a nanorod is substantially uniform along the entire length of the nanorod. A nanorod is solid not hollow.

"Nanostructure" refers to nanotubes, nanorods, and any combinations or mixtures of nanotubes and nanorods.

"Nanotube", "nanofiber" and "fibril" are used interchangeably. Each refers to an elongated hollow structure having a diameter less than 1 μm. The term "nanotube" also includes "bucky tubes" and graphitic nanofibers in which the graphene planes are oriented in herring bone pattern.

"Nitrogenation" means treatment with any compound containing nitrogen.

"Nonuniform pore structure" refers to a pore structure occurring when individual discrete nanotubes are distributed in a substantially nonuniform manner with substantially nonuniform spacings between nanotubes.

Oxycarbides, unlike carbides, are inherently non-stoichiometric. They are any structure containing oxygen predominantly on the surface and derived from a carbide. For example, the oxycarbides of the present invention can have the formula:

$$Q_nC_{x-y}O_y$$
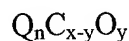
5 wherein Q is as defined above; n and x are selected to satisfy a known stoichiometry of a carbide of Q; y is less than x and the ratio $[y/(x-y)]$ is at least 0.02 and less than 0.9 and more preferably is between 0.05 and 0.50. Furthermore, the term "oxycarbides" also includes, but is not limited to, products formed by oxidative treatments of carbides present in carbon nanotubes used as a source of carbon or in connection with carbide 10 nanorods as a source of carbides. Oxycarbides can also include products formed by carburization of metal oxides. Oxycarbides also comprise mixtures of unreacted carbides and oxides, chemisorbed and physisorbed oxygen. More specifically, oxycarbides have a total amount of oxygen sufficient to provide at least 25% of at least one monolayer of absorbed oxygen as determined by temperature programmed desorption (TPD) 15 containing on the carbide content of the carbide source. Oxycarbides also refer to compounds of the same name as defined in *The Chemistry of Transition Metal Carbides and Nitrides*, edited by S.T. Oyama, a Blackie Academic & Professional Publication. Examples of oxycarbides include polycrystalline compounds, wherein Q is a metal preferably in two valent states. Q can be bonded to another metal atom or only to an 20 oxygen or only to a carbon atom. However, Q is not bonded to both oxygen and carbon atoms. The term "carbides" encompasses both carbides and oxycarbides.

"Oxycarbides-containing nanorod" refers to an Q-containing nanorod having the formula $Q_nC_{x-y}O_y$ as defined above, having an aspect ratio of 5 to 500.

"Physical property" means an inherent, measurable property of the porous 25 structure, e.g., surface area, resistivity, fluid flow characteristics, density, porosity, etc.

"Phosphorylation" means treatment with any compound containing phosphorus.

"Pore" traditionally refers to an opening or depression in the surface of a catalyst or catalyst support. Catalysts and catalyst supports comprising carbon nanotubes lack such traditional pores. Rather, in these materials, the spaces between individual

nanotubes behave as pores, and the equivalent pore size of nanotube aggregates can be measured by conventional methods (porosimetry) of measuring pore size and pore size distribution. By varying the density and structure of aggregates, the equivalent pore size and pore size distribution can be varied.

5   "Q" represents an element selected from the group consisting of transition metals (groups IIIB, IVB, VB , VIB, VIIB, and VIII of periods 4, 5, and 6 of the Periodic Table), rare earths (lanthanides) and actinides. More preferably, Q is selected from the group consisting of Ti, Ta, Nb, Zr, Hf, Mo, V and W

"Q-containing" refers to a compound or composition modified reaction with Q as
10   defined above.

"Relatively" means that 95% of the values of the physical property when measured along an axis of, or within a plane of or within a volume of the structure, as the case may be, will be within plus or minus 20% of a mean value.

"Substantially" or "predominantly" mean that 95% of the values of the physical
15   property when measured along an axis of, or within a plane of or within a volume of the structure, as the case may be, will be within plus or minus 10% of a mean value.

"Surface area" refers to the total surface area of a substance measurable by the BET technique as known in the art, a physisorption technique. Nitrogen or helium can be use absorbents to measure the surface area.

20   "Uniform pore structure" refers to a pore structure occurring when individual discrete nanotubes or nanofibers form the structure. In these cases, the distribution of individual nanotubes in the particles is substantially uniform with substantially regular spacings between the nanotubes. These spacings (analogous to pores in conventional supports) vary according to the densities of the structures.

25   **Carbon Nanotubes**

The term nanotubes refers to various carbon tubes or fibers having very small diameters including fibrils, whiskers, buckytubes, etc. Such structures provide significant surface area when assembled into a structure because of their size and shape. Moreover, such nanotubes can be made with high purity and uniformity.

Preferably, the nanotube used in the present invention have a diameter less than 1 μm, preferably less than about 0.5 μm, and even more preferably less than 0.1 μm and most preferably less than 0.05 μm.

Carbon nanotubes can be made having diameters in the range of 3.5 to 70 nm.

5   The nanotubes, buckytubes, fibrils and whiskers that are referred to in this application are distinguishable from continuous carbon fibers commercially available as reinforcement materials. In contrast to nanofibers, which have desirably large, but unavoidably finite aspect ratios, continuous carbon fibers have aspect ratios (L/D) of at least 10^4 and often 10^6 or more. The diameter of continuous fibers is also far larger than

10   that of fibrils, being always greater than 1 μm and typically 5 to 7 μm.

Continuous carbon fibers are made by the pyrolysis of organic precursor fibers, usually rayon, polyacrylonitrile ("PAN") and pitch. Thus, they may include heteroatoms within their structure. The graphitic nature of "as made" continuous carbon fibers varies, but they may be subjected to a subsequent graphitization step. Differences in degree of

15   graphitization, orientation and crystallinity of graphite planes, if they are present, the potential presence of heteroatoms and even the absolute difference in substrate diameter make experience with continuous fibers poor predictors of nanofiber chemistry.

Carbon nanotubes exist in a variety of forms and have been prepared through the catalytic decomposition of various carbon-containing gases at metal surfaces.

20   U.S. Patent No. 4,663,230 to Tennent hereby incorporated by reference, describes carbon nanotubes that are free of a continuous thermal carbon overcoat and have multiple ordered graphitic outer layers that are substantially parallel to the nanotube axis. As such they may be characterized as having their c-axes, the axes which are perpendicular to the tangents of the curved layers of graphite, substantially perpendicular to their cylindrical

25   axes. They generally have diameters no greater than 0.1 μm and length to diameter ratios of at least 5. Desirably they are substantially free of a continuous thermal carbon overcoat, i.e., pyrolytically deposited carbon resulting from thermal cracking of the gas feed used to prepare them. Tennent describes nanotubes typically 3.5 to 70 nm having an ordered, "as grown" graphitic surface.

U.S. Patent No. 5,171,560 to Tennent et al., hereby incorporated by reference, describes carbon nanotubes free of thermal overcoat and having graphitic layers substantially parallel to the nanotube axes such that the projection of the layers on the nanotube axes extends for a distance of at least two nanotube diameters. Typically, such

5 nanotubes are substantially cylindrical, graphitic nanotubes of substantially constant diameter and comprise cylindrical graphitic sheets whose c-axes are substantially perpendicular to their cylindrical axis. They are substantially free of pyrolytically deposited carbon, have a diameter less than 0.1 μm and a length to diameter ratio of greater than 5. These fibrils are of primary interest in the invention.

10 When the projection of the graphitic layers on the nanotube axis extends for a distance of less than two nanotube diameters, the carbon planes of the graphitic nanotube, in cross section, take on a herring bone appearance. These are termed fishbone fibrils. U.S. Patent No. 4,855,091 to Geus, hereby incorporated by reference, provides a procedure for preparation of fishbone fibrils substantially free of a pyrolytic overcoat.

15 These carbon nanotubes are also useful in the practice of the invention. See also, U.S. Patent No. 5,165,909 to Tennent, hereby incorporated by reference.

Oxidized nanofibers are used to form rigid porous assemblages. U.S. Patent No. 5,965,470, hereby incorporated by reference, describes processes for oxidizing the surface of carbon nanotubes that include contacting the nanotubes with an oxidizing

20 agent that includes sulfuric acid (H_2SO_4) and potassium chlorate ($KClO_3$) under reaction conditions (e.g., time, temperature, and pressure) sufficient to oxidize the surface of the fibril. The nanotubes oxidized according to the processes of McCarthy, et al. are non-uniformly oxidized, that is, the carbon atoms are substituted with a mixture of carboxyl, aldehyde, ketone, phenolic and other carbonyl groups.

25 Nanotubes have also been oxidized nonuniformly by treatment with nitric acid. International Application WO95/07316 discloses the formation of oxidized fibrils containing a mixture of functional groups. Hoogenvaad, M.S., et al. (*Metal Catalysts Supported on a Novel Carbon Support*, Presented at Sixth International Conference on Scientific Basis for the Preparation of Heterogeneous Catalysts, Brussels, Belgium,

30 September 1994) also found it beneficial in the preparation of nanotube-supported

precious metals to first oxidize the nanotube surface with nitric acid. Such pretreatment with acid is a standard step in the preparation of carbon-supported noble metal catalysts, where, given the usual sources of such carbon, it serves as much to clean the surface of undesirable materials as to functionalize it.

5   In published work, McCarthy and Bening (Polymer Preprints ACS Div. of Polymer Chem. 30 (1)420(1990)) prepared derivatives of oxidized nanotubes in order to demonstrate that the surface comprised a variety of oxidized groups. The compounds they prepared, phenylhydrazones, haloaromaticesters, thallous salts, etc., were selected because of their analytical utility, being, for example, brightly colored, or exhibiting
10   some other strong and easily identified and differentiated signal.

Nanotubes may be oxidized using hydrogen peroxide, chlorate, nitric acid and other suitable reagents. See, for example, U.S. Patent Application No. 09/861,370 filed May 18, 2001 entitled "Modification of Carbon Nanotubes by Oxidation with Peroxygen Compounds" and U.S. Patent Application No. 09/358,745, filed July 21, 1999, entitled
15   "Methods of Oxidizing Multiwalled Carbon Nanotubes."

The nanotubes within the structure may be further functionalized as described in U.S. Patent No. 6,203,814 to Fischer.

Carbon nanotubes of a morphology similar to the catalytically grown fibrils or nanotubes described above have been grown in a high temperature carbon arc (Iijima,
20   Nature 354 56 1991, hereby incorporated by reference). It is now generally accepted (Weaver, Science 265 1994, hereby incorporated by reference) that these arc-grown nanofibers have the same morphology as the earlier catalytically grown fibrils of Tennent. Arc grown carbon nanofibers are also useful in the invention.

Nanotube Aggregates and Assemblages

25   The "unbonded" precursor nanotubes may be in the form of discrete nanotubes, aggregates of nanotubes or both.

As with all nanoparticles, nanotubes aggregate in several stages or degrees. Catalytically grown nanotubes produced according to U.S. Patent No. 6,031,711 are formed in aggregates substantially all of which will pass through a 700 μm sieve. About

50% by weight of the aggregates pass through a 300 μm sieve. The size of as-made aggregates can, of course, be reduced by various means.

These aggregates have various morphologies (as determined by scanning electron microscopy) in which they are randomly entangled with each other to form entangled

5   balls of nanotubes resembling bird nests ("BN"); or as aggregates consisting of bundles of straight to slightly bent or kinked carbon nanotubes having substantially the same relative orientation, and having the appearance of combed yarn ("CY") -- e.g., the longitudinal axis of each nanotube (despite individual bends or kinks) extends in the same direction as that of the surrounding nanotubes in the bundles; or, as, aggregates

10   consisting of straight to slightly bent or kinked nanotubes which are loosely entangled with each other to form an "open net" ("ON") structure. In open net structures the extent of nanotube entanglement is greater than observed in the combed yarn aggregates (in which the individual nanotubes have substantially the same relative orientation) but less than that of bird nest. CY and ON aggregates are more readily dispersed than BN.

15   When carbon nanotubes are used, the aggregates, when present, are generally of the bird's nest, combed yarn or open net morphologies. The more "entangled" the aggregates are, the more processing will be required to achieve a suitable composition if a high porosity is desired. This means that the selection of combed yarn or open net aggregates is most preferable for the majority of applications. However, bird's nest

20   aggregates will generally suffice.

The morphology of the aggregate is controlled by the choice of catalyst support. Spherical supports grow nanotubes in all directions leading to the formation of bird nest aggregates. Combed yarn and open nest aggregates are prepared using supports having one or more readily cleavable planar surfaces. U.S. Patent No. 6,143,689 hereby

25   incorporated by reference, describes nanotubes prepared as aggregates having various morphologies.

Further details regarding the formation of carbon nanotube or nanofiber aggregates may be found in the disclosures of U.S. Patent No. 5,165,909; U.S. Patent No. 5,456,897; U.S. Patent No. 5,707,916; U.S. Patent No. 5,877,110; PCT Application No.

30   US89/00322, filed January 28, 1989 ("Carbon Fibrils") WO 89/07163, and Moy et al.,

U.S. Patent No. 5,110,693, U.S. Patent Application Serial No. 447,501 filed May 23,

1995; U.S. Patent Application Serial No. 456,659 filed June 2, 1995; PCT Application

No. US90/05498, filed September 27, 1990 ("Fibril Aggregates and Method of Making

Same") WO 91/05089, and U.S. Patent No. 5,500,200; U.S. Application No. 08/329,774

5   by Bening et al., filed October 27, 1984; and U.S. Patent No. 5,569,635, all of which are

assigned to the same assignee as the invention here and of which are hereby incorporated

by reference.

Nanotube mats or assemblages have been prepared by dispersing nanofibers in

aqueous or organic media and then filtering the nanofibers to form a mat or assemblage.

10   The mats have also been prepared by forming a gel or paste of nanotubes in a fluid, e.g.

an organic solvent such as propane and then heating the gel or paste to a temperature

above the critical temperature of the medium, removing the supercritical fluid and finally

removing the resultant porous mat or plug from the vessel in which the process has been

carried out. See, U.S. Patent No. 5,691,054.

Extrudates of Carbon Nanotubes

15   In a preferred embodiment the carbon rigid porous structures comprise extrudates

of carbon nanotubes. Aggregates of carbon nanotubes treated with a gluing agent or

binder are extruded by conventional extrusion methods into extrudates which are

pyrolyzed or carbonized to form rigid carbon structures. If the bundles of carbon

20   nanotubes are substantially intact except that they have been splayed (e.g. by sonication)

or partially unraveled, the structure provides a bimodal pore structure. The space

between bundles ranges from points of contact to about 1 μm. Within bundles, spaces

between carbon nanotubes range from 10 to 30 nm. The resulting rigid bimodal porous

structure is substantially free of micropores, has surface areas ranging from about 250

25   m^2/gm to about 400 m^2/gm and a crush strength of about 20 psi for extrudates of 1/8 inch

in diameter. Carbon nanotube extrudates have densities ranging from about 0.5 gm/cm^3

to about 0.7 gm/cm^3, which can be controlled by the density of the extrusion paste. The

extrudates have liquid absorption volumes from about 0.7 cm^3/gm.

Gluing or binding agents are used to form the paste of carbon nanotubes required

30   for extrusion processes. Useful gluing or binding agents include, without limitation,

cellulose, carbohydrates, polyethylene, polystyrene, nylon, polyurethane, polyester, polyamides, poly(dimethylsiloxane), phenolic resins and the like.

The extrudates obtained as described above can be further treated with mild oxidizing agents such as hydrogen peroxide without affecting the integrity of the rigid

5 porous carbon structures. Subsequently, the rigid porous structures can be impregnated with catalytic particles by ion exchange, generally a preferred method for deposition of small size particles. Alternatively, the rigid porous carbon structure can also be impregnated with catalysts by incipient wetness, or physical or chemical adsorption.

The rigid, high porosity structures can be formed from regular nanotubes or

10 nanotube aggregates, either with or without surface modified nanofibers (i.e., surface oxidized nanotubes). Surface oxidized nanotubes can be cross-linked according to methods described in U.S. Patent No. 6,031,711 and U.S. Patent No. 6,099,965, and then carbonized to from a rigid porous carbon structure having a uniform pore structure, substantially free of micropores.

Nanorods

15 The term nanorods refers to rod-like structures having a substantially solid core, a surface and a diameter greater than 1 nanometer but less than 100 nm. The structure has an aspect ratio between 5 and 500 and a length between 2 nm and 50 µm and preferably between 100 nm and 20 µm. The disclosed nanorods are substantially solid. They are

20 not hollow with one open end, hollow with two open ends or hollow with two sealed ends.

Carbide Nanorods

Carbide-containing nanorods can be prepared by using carbon nanotubes as a source of carbon. For example, in WO/00/19121 incorporated herein by reference,

25 carbide nanorods were prepared. Q-containing gas was reacted with carbon nanotubes to form, *in situ*, solid Q-containing carbide nanorods at temperatures substantially less than 1700°C and preferably in the range of about 1000°C to about 1400°C, and more preferably at approximately 1200°C. The Q-containing gases were volatile compounds capable of forming carbides.

This conversion is called pseudotopotactic because even though the dimensions and crystalline orientations of the starting material and product differ, the cylindrical geometry of the starting nanotube is retained in the final nanorod and the nanorods remain separate and predominately unfused to each other. The diameters of the resulting

5   nanorods were about double that of the starting carbon nanotubes (1 nm- 100 nm).

Carbide nanorods have also been prepared by reacting carbon nanotubes with volatile metal or non-metal oxide species at temperatures between 500°C and 2500°C wherein the carbon nanotube is believed to act as a template, spatially confining the reaction to the nanotube in accordance with methods described in PCT/US 96/09675 by

10   C.M. Lieber. See also U.S. Patent application Serial Nos. 09/615,350 and 09/481,184 filed July 12, 2000 and January 12, 2000 respectively. Carbide nanorods formed by methods wherein the carbon nanotube serves as a template are also useful in the present invention.

Because of the ease with which they can penetrate fibril aggregates and rigid

15   porous structures, volatile Q compounds are usually preferred. Volatile Q precursors are compounds having a vapor pressure of at least twenty torr at reaction temperature. Reaction with the volatile Q compound may or may not take place through a non-volatile intermediate.

Other methods of preparing carbide nanorods include reductive carburization in

20   which the carbon nanotubes are reacted with Q-containing volatile metal oxides followed by passing a flow of gaseous CH_4/H_2 mixture at temperatures between 250°C and 700°C. In addition to Q-containing metal oxides, volatile Q-containing compounds useful in preparation of Q-containing carbide nanorods include carbonyls and chlorides such as, for example, $Mo(CO)_6$, Mo(V) chloride or W(VI)O chloride.

25   In a preferred method of making useful carbide nanorods for the present invention, vapors of a volatile Q-containing compound are passed over a bed of extrudates of carbon nanotubes in a quartz tube at temperatures from about 700°C to about 1000°C. By controlling the concentration of the Q-containing compound, the crystallization of the carbides is limited to the space of the nanotubes.

In all the methods of providing carbide-containing nanorods discussed above, the extent of conversion of the carbon in carbon nanotubes to carbide nanorods can be controlled by adjusting the concentration of the Q-containing compound, the temperature at which the reaction occurs and the duration of the exposure of carbon nanotubes to the

5   volatile Q-containing compound. The extent of conversion of the carbon from the carbon nanotubes is between 0.5% and 100%, and preferably around 95%. The resulting carbide nanorods have an excellent purity level in the carbide content, vastly increased surface area and improved mechanical strength. The surface area of the carbide nanorods is from 1 to 400 and preferably 10 to 300 m^2/gm.

10   Applications for compositions based on carbide nanorods include catalysts and catalyst supports. For example, compositions including carbide nanorods based on molybdenum carbide, tungsten carbide, vanadium carbide, tantalum carbide and niobium carbide are useful as catalysts in fluid phase reactions.

Similarly, silicon carbide and aluminum carbide-containing nanorods are

15   especially useful as catalyst supports for conventional catalysts such as platinum and palladium, as well as for other Q-containing carbides such as molybdenum carbide, tungsten carbide, vanadium carbide and the like.

Oxycarbide Nanorods

Oxycarbide-containing nanorods can be prepared from carbide nanorods. The

20   carbide nanorods are subjected to oxidative treatments known in the art. For example, oxidative treatments are disclosed in U.S. Patent No. 5,576,466; M. Ledoux, et al. European Pat. Appln. No. 0396 475 A1, 1989; C. Pham-Huu, et al., Ind. Eng. Chem. Res. 34, 1107-1113, 1995; E. Iglesia, et al., *Journal of Catalysis*, 131, 523-544, 1991. The foregoing oxidative treatments are applicable to the formation of oxycarbide nanorods as

25   well as to the formation of nanotubes and/or nanorods comprising an oxycarbide portion wherein the conversion of the carbide source is incomplete.

Oxycarbide compounds present in an oxycarbide nanorod, and also present when the conversion of the carbide source is incomplete, include oxycarbides having a total amount of oxygen sufficient to provide at least 25% of at least 1 monolayer of absorbed

30   oxygen as determined by temperature programmed desorption (TPD) based on the

carbide content of the carbide source. For example, by subjecting carbide nanorods to a current of oxidizing gas at temperatures of between 30°C to 500°C oxycarbide nanorods are produced. Useful oxidizing gases include but are not limited to air, oxygen, carbon dioxide, nitrous oxide, water vapor and mixtures thereof. These gases may be pure or

5   diluted with nitrogen and/or argon.

Compositions comprising oxycarbide nanorods are useful as catalysts in many fluid phase petrochemical and refining processes including hydrogenation, hydrodesulfurisation, hydrodenitrogenation, hydrodemetallisation, hydrodeoxygenation, hydrodearomatization, dehydrogenation, hydrogenolysis, isomerization, alkylation,

10   dealkylation and transalkylation.

Supported Carbides and Oxycarbides

According to another embodiment of the present invention, by adjusting the process parameters, for example, the temperature, the concentration of, and the length of exposure to the Q-containing volatile compound, it is possible to limit the rate of

15   conversion of the carbon in the carbon nanotube. Thus, it is possible to provide carbon nanotubes having a carbide portion where the location of the carbide portion can be engineered as desired. For example, the carbide portion of the carbon nanotube can be located entirely on the surface of the carbon nanotube such that only parts of the surface comprise nanocarbide compounds. It is possible to have the entire surface of the carbon

20   nanotube coated with carbides while the core of the carbon nanotube remains substantially carbon. Moreover, it is possible to control the surface coverage of carbon nanotubes with carbide compounds at from 1% to 99% of the entire surface area. An embodiment wherein the carbon nanotube comprises carbide covering less than 50% of the surface of the carbon nanotube is preferred. Of course, at low percentages large areas

25   of the carbon nanotube surface remain uncovered. Nevertheless, as long as the carbide portion of the carbon nanotube is retained at the surface, the morphology of the carbon nanotube remains substantially the same. Similarly, through careful control of the process parameters, it is possible to turn the carbide portion of the nanotube into a carbide nanorod thereby obtaining a nanotube-nanorod hybrid structure. The carbide portion can

30   be located anywhere on the carbon nanotube. Partial conversion of carbon to carbide

compounds preferably varies from about 20% to about 85% by weight. When the content of carbide compounds in the carbon nanotube exceeds 85% by weight, the carbon nanotubes have been substantially converted to carbide nanorods. Once in possession of the teachings herein, one of ordinary skill in the art can determine as a routine matter and

5   without the need for undue experimentation how to control the rate of conversion of carbon nanotubes to carbide nanorods in order to convert the carbon in the carbon nanotubes incompletely.

       The embodiment of the invention where the carbon nanotubes contain a carbide portion also encompasses providing the carbide portion of the carbon nanotube in any

10   manner now known or later developed. For example, in another method of providing carbide compounds on carbon nanotubes or aggregates thereof, the Q-containing metal or metal compound, preferably molybdenum, tungsten, or vanadium is placed on the carbon nanotubes or aggregates directly and then pyrolyzed, leaving behind carbon nanotubes coated with carbide compounds.

15   In yet another method of providing carbide compounds on carbon nanotubes, solutions of Q-containing salts, such as, for example, salts of molybdenum, tungsten, or vanadium are dispersed over the carbon nanotubes or aggregates thereof and then pyrolyzed, again forming carbide compounds primarily on the surface of the carbon nanotubes.

20   An embodiment wherein the core of the carbon nanotube remains carbon and the location of the metallic carbides is limited is quite desirable as a catalytic system. The core of the carbon nanotube acts as a catalyst support or carrier for the metallic carbide catalyst.

       In yet another embodiment of the improvement discussed above, it is possible to

25   subject the nanotube having a carbide portion to oxidative treatments such that the carbide portion of the nanotube further comprises an oxycarbide portion. The oxycarbide portion comprises oxycarbide compounds located any place on, in and within the carbon nanotube or carbide nanorod.

The oxycarbide compounds can be placed on the nanotube in any way now known or later developed. Similarly, the nanotube having a carbide portion can be exposed to air or subjected to carburization or any other means of converting the carbide portion of the nanotube partially or completely into an oxycarbide nanorod portion.

5 Thus, it is possible to provide a carbon nanotube which is partly still a carbon nanotube, partly a carbide nanorod and partly an oxycarbide nanorod. This may be referred to as a carbon-carbide-oxycarbide nanotube-nanorod hybrid.

Carbide and Oxycarbide Rigid Porous Structures

The invention also relates to rigid porous structures made from carbide nanorods, 10 oxycarbide nanorods, and supported carbide and oxycarbide carbon nanotubes and methods for producing the same. The resulting structures may be used in catalysis, chromatography, filtration systems, electrodes, batteries and the like.

The rigid porous structures according to the invention have high accessible surface area. That is, the structures have a high surface area which is substantially free of 15 micropores. The invention relates to increasing the mechanical integrity and/or rigidity of porous structures comprising intertwined carbon nanotubes and/or carbide and/or oxycarbide nanorods. The structures made according to the invention have higher crush strengths than the conventional carbon nanotube or nanorod structures. The present invention provides a method of improving the rigidity of the carbon structures by causing 20 the nanotubes and/or nanorods to form bonds or become glued with other nanotubes and/or nanorods at the nanotube and/or nanorod intersections. The bonding can be induced by chemical modification of the surface of the nanotubes to promote bonding, by adding "gluing" agents and/or by pyrolyzing the nanotubes to cause fusion or bonding at the interconnect points.

25 The nanotubes or nanorods can be in the form of discrete nanotubes and/or nanorods or aggregate particles of nanotubes and nanorods. The former results in a structure having fairly uniform properties. The latter results in a structure having two-tiered architecture comprising an overall macrostructure comprising aggregate particles of nanotubes and/or nanorods bonded together and a microstructure of intertwined 30 nanotubes and/or nanorods within the individual aggregate particles.

According to one embodiment, individual discrete nanotubes and/or nanorods form the structure. In these cases, the distribution of individual nanotube and/or nanorod strands in the particles are substantially uniform with substantially regular spacing between strands. These spacings (analogous to pores in conventional supports) vary according to the densities of the structures and range roughly from 15 nm in the densest to an average 50 to 60 nm in the lightest particles (e.g., solid mass formed from open net aggregates). Absent are cavities or spaces that would correspond to micropores in conventional carbon supports.

According to another embodiment, the distribution of individual nanotubes and/or nanorods is substantially nonuniform with a substantially nonuniform pore structure. Nevertheless, there are no cavities or spaces corresponding to micropores which are frequently present in other catalysts and catalyst supports.

These rigid porous materials are superior to currently available high surface area materials for use in fixed-bed reactors, for example. The ruggedness of the structures, the porosity (both pore volume and pore structure), and the purity of the carbide nanorods and/or oxycarbide nanorods are significantly improved. Combining these properties with relatively high surface areas provides a unique material with useful characteristics.

One embodiment of the invention relates to a rigid porous structure comprising carbide nanorods having an accessible surface area greater than about 10 m^2/gm and preferably greater than 50 m^2/gm, being substantially free of micropores and having a crush strength greater than about 1 lb. The structure preferably has a density greater than 0.5 gm/cm^3 and a porosity greater than 0.8 cm^3/gm. Preferably, the structure comprises intertwined, interconnected carbide nanorods and is substantially free of micropores.

According to one embodiment, the rigid porous structure includes carbide nanorods comprising oxycarbide compounds, has an accessible surface area greater than about 10 m^2/gm, and preferably greater than 50 m^2/gm, is substantially free of micropores, has a crush strength greater than about 1 lb and a density greater than 0.5 gm/cm^3 and a porosity greater than 0.8 cm^3/gm.

According to another embodiment the rigid porous structure includes oxycarbide nanorods having an accessible surface area greater than about 10 m^2/gm, and preferably greater than 50 m^2/gm, being substantially free of micropores, having a crush strength greater than about 1 lb, a density greater than 0.5 gm/cm^3 and a porosity greater than 0.8 cm^3/gm.

According to yet another embodiment, the rigid porous structure includes carbon nanotubes comprising a carbide portion. The location of the carbide portion can be on the surface of the carbon nanotube or any place on, in or within the carbon nanotube or the carbide portion can be converted into a carbide nanorod forming a carbon nanotube-carbide nanorod hybrid. Nevertheless, the catalytic effectiveness of these rigid porous structures is not affected by the carbide portion on the resulting composites. This rigid porous structures has an accessible surface area greater than about 10 m^2/gm and preferably than 50 m^2/gm, is substantially free of micropores, has a crush strength greater than about 1 lb, a density greater than 0.5 gm/cm^3 and a porosity greater than 0.8 cm^3/gm.

In another related embodiment the rigid porous structure includes carbon nanotubes having a carbide portion and also an oxycarbide portion. The location of the oxycarbide portion can be on the surface of the carbide portion or any place on, in or within the carbide portion.

Under certain conditions of oxidative treatment it is possible to convert a portion of the carbide nanorod part of the carbon-carbide nanotube-nanorod hybrid into an oxycarbide. The rigid porous structure incorporating carbon-carbide-oxycarbide nanotube-nanorod hybrids has an accessible surface area greater than about 10 m^2/gm, is substantially free of micropores, has a crush strength greater than about 1 lb, a density greater than 0.5 gm/cm^3 and a porosity greater than 0.8 cm^3/gm.

According to one embodiment, the rigid porous structures described above comprise nanotubes and/or nanorods which are uniformly and evenly distributed throughout the rigid structures. That is, each structure is a rigid and uniform assemblage of nanotubes and/or nanorods. The structures comprise substantially uniform pathways and spacings between the nanotubes and/or nanorods. The pathways or spacings are uniform in that each has substantially the same cross-section and are substantially evenly

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spaced. Preferably, the average distance between nanotubes and/or nanorods is less than about 0.03 μm and greater than about 0.005 μm. The average distance may vary depending on the density of the structure.

5   According to another embodiment, the rigid porous structures described above comprise nanotubes and/or nanorods which are nonuniformly and unevenly distributed throughout the rigid structures. The rigid structures comprise substantially nonuniform pathways and spacings between the nanorods. The pathways and spacings have nonuniform cross-section and are substantially unevenly spaced. The average distance between nanotubes and/or nanorods varies between 0.0005 μm to 0.03 μm. The average

10   distances between nanotubes and/or nanorods may vary depending on the density of the structure.

According to another embodiment, the rigid porous structure comprises nanotubes and/or nanorods in the form of nanotube and/or nanorod aggregate particles interconnected to form the rigid structures. These rigid structures comprise larger

15   aggregate spacings between the interconnected aggregate particles and smaller nanotube and/or nanorod spacings between the individual nanotubes and/or nanorods within the aggregate particles. Preferably, the average largest distance between the individual aggregates is less than about 0.1 μm and greater than about 0.001 μm. The aggregate particles may include, for example, particles of randomly entangled balls of nanotubes

20   and/or nanorods resembling bird nests and/or bundles of nanotubes and/or nanorods whose central axes are generally aligned parallel to each other.

Another aspect of the invention relates to the ability to provide rigid porous particulates or pellets of a specified size dimension. For example, porous particulates or pellets of a size suitable for use in a fluidized packed bed. The method involves

25   preparing a plurality of nanotubes and/or nanorods aggregates, fusing or gluing the aggregates or nanotubes and/or nanorods at their intersections to form a large rigid bulk solid mass and sizing the solid mass down into pieces of rigid porous high surface area particulates having a size suitable for the desired use, for example, to a particle size suitable for forming a packed bed.

General Methods of Making Rigid Porous Structures

The above-described rigid porous structures are formed by causing the nanotubes and/or nanorods to form bonds or become glued with other nanofibers at the fiber intersections. The bonding can be induced by chemical modification of the surface of the

5 nanofibers to promote bonding, by adding "gluing" agents and/or by pyrolyzing the nanofibers to cause fusion or bonding at the interconnect points. U.S. Patent No. 6,099,965 to Tennent describes processes for forming rigid porous structures from carbon nanotubes. These processes are equally applicable to forming rigid porous structures including discrete unstructured nanotubes or nanotube aggregates comprising carbides

10 and in another embodiment also oxycarbides, wherein the carbon nanotube morphology has been substantially preserved. These methods are also applicable to forming rigid porous structures comprising carbide or oxycarbide nanorods, unstructured or as aggregates. Additionally, these methods are also applicable to forming rigid porous structures comprising hybrids of carbon-carbide nanotube-nanorods and/or carbon-

15 carbide-oxycarbide nanotube-nanorods.

In several other embodiments rigid porous structures comprising carbide nanorods are prepared by contacting a rigid porous carbon structure made of carbon nanotubes with volatile Q-containing compounds under conditions sufficient to convert all of the carbon or only part of the carbon of the carbon nanotubes to carbide-containing compounds.

20 ## Methods of Making Carbide Containing Rigid Porous Structures

There are many methods of preparing rigid porous structures comprising carbide nanorods. In one embodiment the rigid porous carbon structures prepared as described above are contacted with Q-containing compounds under conditions of temperature and pressure sufficient to convert the carbon nanotubes of the rigid porous carbon structure to

25 carbide nanorods. The carbide portion of the carbon nanotubes of the rigid porous structure can be on the surface of the carbon nanotube or at any place on, in or within the carbon nanotube. When the conversion is complete, the entire carbon nanotube is transformed into a substantially solid carbide nanorod. Once in the possession of the teachings herein, one of ordinary skill in the art can determine as a routine matter and

30 without the need for undue experimentation how to control the rate of conversion of

carbon nanotubes present in the rigid porous carbon structure to a rigid porous carbide-containing structure comprising carbon nanotubes having a carbide portion located at various places on the carbon nanotube present in an amount from about 20% to about 85%, preferably in excess of 85% by weight.

5   The carbide-containing rigid porous structures of the present invention have high accessible surface areas between 10 m^2/gm and 100 m^2/gm and are substantially free of micropores. These structures have increased mechanical integrity and resistance to attrition in comparison to individual carbide-containing nanorods. Carbide-containing rigid porous structures have a density greater than 0.5 gm/cm^3 and a porosity greater than 10   0.8 cm^3/gm. The structure has at least two dimensions of at least 10 μm and not greater than 2 cm. Depending on the pore structure of the starting rigid porous carbon structure, the structure of the carbide-containing rigid porous structure can be uniform, nonuniform or bimodal.

When the rigid porous structure is uniform the average distance between the 15   carbide-containing nanorods is less than 0.03 μm and greater than 0.005 μm. In another embodiment the rigid porous structure comprises carbide-containing nanorods in the form of interconnected aggregate particles wherein the distance between individual aggregates ranges from point of contact to 1 μm. When the carbide-containing nanorod rigid porous structures are formed from rigid porous carbon structures comprising nanotube 20   aggregates, the structure has aggregate spacings between interconnected aggregate particles and carbide nanorod spacings between nanorods within the aggregate particles. As a result the rigid porous structure has a bimodal pore distribution.

One embodiment of the invention relates to rigid porous structures comprising extrudates of aggregate particles of carbide nanorods, wherein the carbide nanorods are 25   glued together with binding agents such as cellulose, carbohydrates, polyethylene, polystyrene, nylon, polyurethane, polyester, polyamides, poly(dimethylsiloxane) and phenolic resins. Without being bound by theory, it is believed that the conversion of a rigid porous carbon structure to a carbide-containing rigid porous structure, whether completely or partially, is accomplished in pseudotopotactic manner as previously 30   discussed.

Methods of Making Oxycarbide Containing Rigid Porous Structures

There are many methods of preparing rigid porous structures comprising oxycarbide nanorods and/or nanotubes comprising a carbide portion and an oxycarbide portion. In one embodiment the carbide containing rigid porous structures are subjected

5   to oxidative treatments as disclosed in the art and in U.S. Patent No. 5,576,466.

In another embodiment rigid porous structures comprising carbon nanotubes having an oxycarbide portion and/or a carbide portion are prepared by subjecting rigid porous carbon structures which have been partially converted to carbide nanorods to oxidative treatments disclosed in the art.

10   In another embodiment discrete carbide nanorods are subjected to oxidative treatments and then assembled into rigid porous structures according to methods similar to those disclosed in U.S. Patent No. 6,099,965.

In yet another embodiment discrete carbon nanotubes or aggregate of carbon nanotubes which have been partially converted to carbide nanorods are further subjected

15   to oxidative treatments and then assembled into rigid porous structures according to methods disclosed in U.S. Patent No. 6,099,965.

Catalytic Compositions

The carbide and/or oxycarbide nanorods and nanotubes having carbide and/or oxycarbide portions of the invention, have superior specific surface areas as compared to

20   carbide and oxycarbide catalysts previously taught in the art. As a result, they are especially useful in the preparation of catalysts and as catalyst supports in the preparation of supported catalysts. The catalysts of the invention include catalytic compositions comprising nanotubes and/or nanorods and rigid porous structures comprising the same. These "self-supported" catalysts of the invention constitute the active catalyst compound

25   and can be used with or without any additional physical support to catalyze numerous heterogeneous, fluid phase reactions as more specifically described herein. The supported catalysts of the invention comprise a support including a nanofiber and/or nanorod rigid porous structure and a catalytically effective amount of a catalyst supported thereon. The catalytic compositions can contain from about 10% to 95% carbides by

weight of the composition. The catalyst compositions can further include from about 0.5% to 25% oxycarbides by weight of the carbides of the composition.

The uniquely high macroporosity of carbon nanotube or carbide nanorod structures, the result of their macroscopic morphology, greatly facilitates the diffusion of reactants and products and the flow of heat into and out of the self-supported catalysts. This unique porosity results from a random entanglement or intertwining of nanotubes and/or nanorods that generates an unusually high internal void volume comprising mainly macropores in a dynamic, rather than static state. Ease of separation of these catalysts from the fluid phase and lower losses of these catalyst as fines also improves process performance and economics. Other advantages of the nanotube and/or nanorod structures as self-supported catalysts include high purity, improved catalyst loading capacity and chemical resistance to acids and bases. As self-supported catalysts, carbon nanotube and/or nanorod aggregates have superior chemical and physical properties in respect of their porosity, surface area, separability and purity.

Self-supported catalysts made of nanotubes and/or nanorods have a high internal void volume that ameliorates the plugging problem encountered in various processes. Moreover, the preponderance of large pores obviates the problems often encountered in diffusion or mass transfer limited reactions. The high porosities ensure significantly increased catalyst life.

One embodiment of the invention relates to a self-supported catalyst which is a catalytic composition comprising carbide-containing nanorods having a diameter between at least 1 nm and less than 100 nm, and preferably between 3.5 nm and twenty nm. The carbide-containing nanorods have been prepared from carbon nanotubes which have been substantially converted to carbide nanorods. In the catalytic compositions of this embodiment the carbide nanorods retain substantially the structure of the original carbon nanotubes. Thus, the carbide nanotubes can have uniform, nonuniform or bimodal porous structures. These catalytic compositions can be used as catalysts to catalyze reactions such as hydrogenation, hydrodesulfurisation, hydrodenitrogenation, hydrodemetallisation, hydrodeoxygenation, hydrodearomatization, dehydrogenation, hydrogenolysis, isomerization, alkylation, dealkylation and transalkylation.

Catalytic Compositions Supported on Aggregates of Carbide and Oxycarbide Nanorods

Depending upon the application, the rigid porous structures of the invention can be used as both self-supported catalysts and as catalyst supports. As is true of catalysts comprising regular nanotubes and/or nanorods, catalysts and catalyst supports comprising the rigid porous structures of the invention have unique properties. They are relatively free of micropores. They are also pure and resistant to attrition, compression and shear. Consequently, they can be easily separated from a fluid phase reaction medium and after a long service life. The rigid porous structures of the invention can be used as catalysts and catalyst supports in a variety of fixed bed catalytic reactions.

Rigid structures formed from nanorod aggregates, preferably silicon carbide and aluminum carbide-containing nanorods, are particularly preferred structures for use as catalyst supports.

The combination of properties offered by nanorod structures is unique. Known catalyst supports do not have such high porosity, high accessible surface area and attrition resistance. This combination of properties is advantageous in any catalyst system amenable to the use of a carbide catalyst support. The multiple nanorods that make up a nanorod structure provide a large number of junction points at which catalyst particles can bond to the structures. This provides a catalyst support that tenaciously holds the supported catalyst. Further, nanorod structures permit high catalyst loadings per unit weight of nanorod. Catalyst loadings are generally greater than 0.01 weight percent and preferably greater than 0.1, but generally less than 5% weight containing on the total weight of the supported catalyst. Typically catalyst loadings greater than 5% by weight are not useful, but such catalyst loadings are easily within the contemplation of the invention, as are loadings in excess of 50 weight percent containing of the total weight of the supported catalyst.

Desirable hydrogenation catalysts which can be supported on the nanorod and/or nanotube structures of the invention are the platinum group of metals (ruthenium, osmium, rhodium, iridium, palladium and platinum or a mixture thereof), preferably

palladium and platinum or a mixture thereof. Group VII metals including particularly iron, nickel and cobalt are also attractive hydrogenation catalysts.

Oxidation (including partial oxidation) catalysts may also be supported on the nanotube and/or nanorod structures. Desirable metallic oxidation catalysts include, not

5 only members of the platinum group enumerated above, but also, silver and the group VIII metals. Oxidation catalysts also include metal salts known to the art including salts of vanadium, tellurium, manganese, chromium, copper, molybdenum and mixtures thereof as more specifically described in *Heterogeneous Catalytic Reactions Involving Molecular Oxygen*, by Golodets, G.I. & Ross, J.R.H, *Studies in Surface Science*, 15,

10 Elsevier Press, NYC 1983.

Active catalysts include other carbide compounds such as carbides of titanium, tantalum, hafnium, niobium, zirconium, molybdenum, vanadium and tungsten. These carbides are particularly useful for hydrogenation, hydrodesulfurisation, hydrodenitrogenation, hydrodemetallisation, hydrodeoxygenation, hydrodearomatization,

15 dehydrogenation, hydrogenolysis, isomerization, alkylation, dealkylation and transalkylation.

Because of their high purity, carbide nanorod aggregates exhibit high resistance to attack by acids and bases. This characteristic is advantageous since one path to regenerating catalysts is regeneration with an acid or a base. Regeneration processes can

20 be used which employ strong acids or strong bases. This chemical resistance also allows the carbide supports of the invention to be used in very corrosive environments.

Preparation of Supported Catalysts

Supported catalysts are made by depositing a catalytically effective amount of catalyst on the rigid nanorod and/or nanotube structure. The term "on the nanotube

25 and/or nanorod structure" embraces, without limitation, on, in and within the structure and on the nanotubes and/or nanorods thereof. These terms may be used interchangeably. The catalyst can be incorporated onto the nanotube and/or nanorod or aggregates before the rigid structure is formed, while the rigid structure is forming (i.e., it can be added to the dispersing medium) or after the rigid structure is formed.

Methods of depositing the catalyst on the support include adsorption, incipient wetness, impregnation and precipitation. Supported catalysts may be prepared by either incorporating the catalyst onto the aggregate support or by forming it *in situ* and the catalyst may be either active before it is deposited in the aggregate or it may be activated

5   *in situ.*

Catalysts such as a coordination complexes of catalytic transition metals, e.g., palladium, rhodium or platinum, and a ligand, such as a phosphine, can be adsorbed on a support by slurrying nanorods in a solution of the catalyst or catalyst precursor for an appropriate time to achieve the desired loading.

10   These and other methods may be used in forming the catalyst supports. A more detailed description of suitable methods for making catalyst supports using nanotube structures is set forth in U.S. Patent No. 6,099,965.

Catalytic Compositions and Their Uses

The above described catalytic compositions are suited for use in fluid phase

15   reactions such as hydrogenation, hydrodesulfurisation, hydrodenitrogenation, hydrodemetallisation, hydrodeoxygenation, protonation, hydrodearomatization, dehydrogenation, hydrogenolysis, isomerization, alkylation, dealkylation, and transalkylation.

Modification of Catalytic Compositions

20   Catalytic compositions based on carbon nanotubes or carbide nanorods containing carbides and/or oxycarbides can be further modified to create catalytic compositions that are bifunctional. For example, in an embodiment of the invention, the catalytic composition contains multiple active sites. One active site can catalyze a hydrogenation or dehydrogenation reaction. Another active site can catalyze protonation or

25   isomerization reactions. These sites can be created, for example, by an acidification treatment using a strong acid. The term "strong acid" refers to the capability of the reagent to intensely attract electrons.

Catalysts containing carbide nanorods that include carbides and/or oxycarbides or containing carbon nanotubes that include carbides and/or oxycarbides can be modified by

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acidification. Acidification of these catalysts can be accomplished by the incorporation of electron acceptors into the carbon portion of the carbon nanotubes or carbide nanorods, the carbide portion of the carbon nanotubes or carbide nanorods, the oxycarbide carbon nanotubes or carbide nanorods, or any combination thereof. Thus, the acidic sites can

5   reside on the carbon portions and/or the carbide portions and/or the oxycarbide portions. Examples of electron acceptors include, but are not limited to, halogens, nitrogen, sulfur and phosphorus.

In an embodiment of the invention, acidification of the catalytic compositions is accomplished by halogenation. Suitable halogens include fluorine, chlorine, bromine, or

10   iodine. The halogen can also be incorporated using a compound or ion containing a halogen, e.g., ClO_3^-, HCl, CCl_4, $CHCl_3$, or $AlCl_3$, etc.

Prior to the acidification treatment, samples of Q-containing carbides, for example molybdenum carbide or tungsten carbide, can be first passivated, or oxygenated, by oxygen. For example, a gas ratio of 3% oxygen and 97% argon can be passed over the

15   samples in order to passivate them. As a result, a minor component of QO_2, or QO_x wherein x is between 1 and 3, is present in the Q-containing carbide samples.

The Q-containing carbide can be placed in a micro-reactor or an autoclave reactor. The reaction temperature can be raised to a temperature at which the samples are dried. The temperature can range from about 110°C to about 300°C, e.g., 200°C. During

20   the drying process, the samples are blanketed under argon. The argon blanket is then replaced by a carrier gas that contains from about 0.5% to about 10% of Cl_2. The carrier gas chlorinates the samples. The chlorination procedure should be carried out under Cl_2/Ar at temperatures in the range of 500°C to 850°C, e.g., 600°C for, e.g. 1 hour.

Carbon tetrachloride can be used to chlorinate the samples. When using CCl_4 to

25   chlorinate, argon is passed through a gas-liquid saturator that contains pure CCl_4. The temperature of the saturator should be kept at 0 °C by, for example, an ice-water bath. The chlorination procedure is then performed under CCl_4/Ar vapor at 200 to 300°C for a period of time, e.g. 1 hour.

Before the chlorination procedure, the samples can also be heated in hydrogen at a temperature up to about 500 °C to remove the surface oxygen atoms and create anion vacancies to facilitate further incorporation of chlorine. After the hydrogen treatment, the sample is chlorinated.

5   In another embodiment of the invention, sulfation is used. Any compound capable of sulfation can be used, e.g., a sulfate or persulfate containing compound.

Instead of modifying the surface of the catalyst supports, the modification can be made directly to the carbide phase of the Q-containing catalysts. For example, the carbide phases of the Q-containing catalysts can be treated with an acidifying compound.

10   The treatment results in the substitution of halogen, nitrogen, phosphorus, and/or oxygen into the carbide structure of the Q-containing catalysts. A skin is formed having a formula of $MoCl_x$, MoO_xCl_y, MoN_x, MoO_xN_y, MoP_x, or MoO_xC_y where x and y are indefinite numbers representing stoichiometric or non-stochiometric compositions. The presence of the skin alters the acidity of the Q-containing catalyst.

15   For example to acidify the carbide phase of a Q-containing catalyst, nitrogen from NH_3 can be used by heating the NH_3 with the Q-containing catalyst to a temperature from 500°C to 850°C.

In yet another embodiment of the invention acidification of the catalytic compositions can be accomplished by the addition of solid acids into the interstitial positions between the carbon nanotubes and supported carbides. Alternatively, the solid acids can be physically incorporated onto the surface of the rigid porous structures formed from carbide nanorods or nanotubes. The term "solid acid" refers to solid Lewis Acids. Examples of solid acids include, but are not limited to, chlorinated, sulfated, or phosphated compounds containing aluminum or zirconium. The solid acids can be incorporated into the catalytic compositions by incipient wetness or other appropriate technique known in the art. The solid acids can be incorporated before or after calcination.

Modified catalytic compositions are suitable for use in fluid phase reactions including, but not limited to, hydrogenation, hydrodesulfurisation, hydrodenitrogenation,

hydrodemetallisation, hydrodeoxygenation, hydrodearomatization, dehydrogenation, hydrogenolysis, protonation, isomerization, alkylation, dealkyation and transalkylation. For example, the modified catalytic compositions can be used in the isomerization of alkanes, e.g., butane.

5   The acidities of the modified catalytic compositions can be measured by means known in the art. For example, temperature programmed desorption can be used. Temperature programmed desorption is a technique used to examine the surface properties of solid materials. Typically, a small amount of catalyst (10-200 mg) is placed in a reactor that can be heated by a furnace. An inert gas, usually helium or argon at

10   atmospheric pressure, is passed over the catalyst. Following pretreatment to obtain a "clean" catalyst, a gas is adsorbed on the surface, usually by pulse injections of adsorbate into the carrier gas upstream of the reactor. After excess gas is flushed out, the catalyst is heated at a rate such that its temperature rises linearly with time. A small thermocouple inserted in the catalyst measures the temperature and a detector downstream measures the

15   change in the inert gas stream. The ideal detector is a mass spectrometer which measures the composition of the effluent stream as a function of catalyst temperature. Because of the high carrier gas flow rate, the detector response is proportional to the rate of desorption if diffusion and reabsorption are not limiting. By adsorbing acidic or basic gas molecules followed by desorbing upon heating, one can measure the intensity and

20   quantity of the adsorption and thereby characterize the surface properties such as acidity or basicity. Ammonia is a molecule commonly used to measure the acidity of a solid surface. A weak acid usually desorbs at approximately 100°C and a strong acid usually desorbs at temperatures higher than 100°C. Strong acidity is also associated with large quantities of adsorption of ammonia.

25   **Isomerization Reactions Using Modified Carbide or Oxycarbide Catalysts**
           Modified carbide and/or oxycarbide catalysts can use advantages to use to catalyze isomerization reactions, such as the isomerization of alkanes. Any straight-chain, branched or cyclic alkane can be employed as a feed hydrocarbon in the isomerization process. Examples of alkanes which can be isomerized include, but are not

30   limited to, n-butane, n-pentane, n-hexane, 2-methylpentane, 3-methylpentane, n-heptane,

2-methylhexane, 3-methylhexane, octanes, nonanes, decanes and combinations thereof. Alkenes, or olefins, can also be isomerized using the catalysts.

Any suitable isomerization conditions can be employed in the process of the invention. A feed hydrocarbon and a carrier gas such as hydrogen are premixed to create

5   an isomerization feed stream which is then charged to an isomerization zone, i.e., a vapor phase reactor vessel. The feed stream contacts a modified catalytic composition of the invention that has been placed within the reactor vessel.

The effluent from the reactor vessel is subjected to suitable separation techniques as known in the art, to separate the desired isomer product from reactants and by-

10   products.

For example, in the isomerization of normal butane to isobutane, the following process can be used. A vapor phase reactor can be constructed by assembling a thermowell through an end of a vertical quartz tube. A vertical quartz tube with a 12 mm outer diameter can be fitted with a 6 mm quartz thermowell. At the tip of the thermowell,

15   is a porous plug of quartz wool. This porous plug can be used to support the catalyst and/or the catalyst support containing the catalyst. The entire tube is then placed in a tube furnace, for example a ½ -inch tube furnace, in a vertical orientation. The top of the tube is fitted with inlet lines for the feed stream of reactant gases. At the bottom of the tube is an exit line connected to a pressure gauge, e.g., a gauge measuring pressure

20   between 0 and 15 psi. Mass flow controllers are placed in the gas inlet lines to control the flow of reactant gases into the reactor. Suitable mass flow controllers include those manufactured by Allborg Instruments and Controls of Orangeburg, NY.

Ground catalyst or supported catalyst is placed onto the quartz wool plug. The catalytic composition is then treated with hydrogen and argon gas. Thereafter, the

25   catalytic composition can be treated with oxygen and argon gas.

Mixtures of the gas to be isomerized, e.g., n-butane, and hydrogen in molar ratios of about 1:16 to 1:4 of n-butane:H_2 are introduced into the vapor phase reactor at WHSVs of 1-10 h^{-1}. Temperatures and pressures for the reaction can range from 100 °C to about 400 °C, and 1 to about 10 psi, respectively.

Product gases are fed through a gas sampling valve. Gas chromatography ("GC") can be used to analyze the composition of the product gas and determine the conversion and selectivity of the reaction. For example, a Varian gas chromatograph equipped with a GS-Q capillary column can be used to measure C_1-C_5 alkanes and olefins. The

5 capillary columns can be obtained from Alltech Associates of Deerfield, Illinois.

EXAMPLES

The examples are illustrative and not to be considered restrictive of the scope of the invention. Numerous changes and modification can be made with respect to the invention. The materials used in the examples herein are readily commercially available.

10 In all of the experiments which follow, aggregates of carbon nanotubes as manufactured by Hyperion Catalysis International of Cambridge, Massachusetts were used. The aggregates of carbon nanotubes were of the cotton candy ("CC") morphology also known as combed yarn ("CY") as described in the section entitled "Nanotube Aggregates and Assemblages".

15 ## EXAMPLE 1

Preparation of Molybdenum Carbide Precursors by Impregnation of Carbon Nanotube
Aggregates with Molybdenum Acetyl Acetonate

Five gms of powder samples of CC aggregates having porosity of 6.5 cc/gm were impregnated by the incipient wetness method with 35 cc of an ethanol solution containing

20 the correct amount of $MoO_2(C_5 H_7 O_2)_2$ or (molybdenum acetyl acetonate, referred to as Moacac) necessary for the desired C:Mo atom ratio loading. The resulting mixture was dried at 110°C at full vacuum for 18 hours during which the Mo precursor decomposed to a mixture of molybdenum suboxides, generally designated as MoO_{3-x}, wherein x is 0 or 1. The sample was set aside for conversion to carbide catalysts by careful calcination under

25 an inert atmosphere as described in Examples 5, 6 or 7 below.

EXAMPLE 2

Preparation of Molybdenum Carbide Precursors by Impregnation
of Carbon Nanotube Aggregates with Ammonium Molybdate

A similar procedure as used in Example 1 above was followed, except that the

30 impregnating solutions were aqueous solutions containing the correct amount of

ammonium heptamolybdate tetrahydrate $((NH_4)_6Mo_7 O_{24} \cdot 4H_2O$, referred to as

ammonium molybdate) necessary for the desired C:Mo atom ratio loading. The resulting

mixtures were dried at 225°C in full vacuum for 18 hours during which the

heptamolybdate compound was decomposed to MoO_3. The sample was set aside for

5   conversion to carbide catalysts by careful calcination under an inert atmosphere as more

particularly described in Examples 5, 6 and 7 herein.

EXAMPLE 3

Preparation of Molybdenum Carbide Extrudate Precursors by Impregnation with Molybdenum Acetyl Acetonate or Ammonium Molybdate

10   CC or CY type aggregates were oxidized with nitric acid as described in U.S.

Patent No. 6,203,814 to Fischer to form oxidized CC aggregates having an acid titer of

about 0.6 meq/gm.

Five gms of the oxidized CC type aggregates of carbon nanotubes were well-

mixed with either an ethanol solution of Moacac or an aqueous solution of ammonium

15   heptamolybdate tetrahydrate, each solution containing the correct amount of Mo

compound necessary for the desired C:Mo loading. The mixing was accomplished by

kneading in a Braybender kneader until the paste had a homogeneous consistency. The

excess solvent was removed from the kneaded sample by evaporation until a solids

content of from about 8 to about 10% by weight was obtained. The material was then

20   extruded by using a pneumatic gun extruder. The extrudates were about 1/8" in diameter

and several centimeters in length. The extrudates were then dried at 200°C in air for 18

hours during which some shrinkage occurred. The dried extrudates were then broken into

pieces of about 1/16" by ¼" which were set aside for conversion to carbide catalysts by

careful calcination as described in Examples 5, 6 and 7 herein.

25   ## EXAMPLE 4

Preparation of Molybdenum Carbide Precursor by Mixing Carbon Nanotube Aggregates With Ammonium Molybdate or Molybdenum Oxide

As grown CC or CY aggregates were oxidized with nitric acid as described in

Example 3 to form oxidized CC aggregates having an acid titer of about 0.6 meq/gm.

30   Five gms of oxidized CC type aggregates of carbon nanotubes were physically

admixed with the correct amount of either ammonium heptamolybdate tetrahydrate or

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MoO_3 necessary for the desired C:Mo atom ratio by kneading the sample in a mortar and pestle. A small amount of wetting agent such as water or ethylene glycol, was added periodically to keep the oxidized carbon nanotube powder dusting under control and to facilitate the contact between the molybdenum precursor particles and the carbon

5 nanotube aggregates. After the mix was kneaded to a homogeneous thick paste, the excess solvent was removed by gentle warming while continuing to knead the sample. The mixture was then dried at 200°C for 14 hours in air and set aside for conversion to carbide by careful calcination as described in Examples 5, 6 and 7 herein.

EXAMPLE 5

10 Calcination of Molybdenum Carbide Precursors at 600°C or 625°C

Weighed samples of molybdenum carbide precursors, as prepared in Examples 1-4 were loaded into porcelain boats which were then placed horizontally in a one-inch quartz tube. The tube and boat assembly were placed in a high temperature furnace equipped with a programmable temperature controller and a movable thermocouple. The

15 thermocouple was located directly in contact with the end of the boat. The sample was heated under a slow flow, i.e., at several standard cc's/min of argon at a heating rate of 5°C/min to 200°C and thereafter at 1°C/min to the final temperature of 600°C or 625°C. The sample was held at this temperature for 18 hours. Since pure Mo_2C reacts violently with atmospheric oxygen, after cooling in argon to ambient temperature, the samples

20 were passivated by passing 3% O_2/Ar over them for 1 hour. XRD phase analysis indicated that the precursors have converted into β-Mo_2C and/or γ-Mo_2C with minor component of MoO_2.

EXAMPLE 6

Calcination of Molybdenum Carbide Carbon Precursors at 800°C

25 The same procedure as described in Example 5 above was followed up to 600°C. The samples were then held at 600°C for 1 hour. Thereafter, heating was resumed at the same rate of 1°C/min to 800°C and held at that temperature for another 3 hours. After cooling in argon, the samples were passivated using 3% O_2/Ar. XRD phase analysis indicated that the precursors have converted into β-Mo_2C.

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EXAMPLE 7

Calcination of Molybdenum Carbide Carbon Precursors at 1000°C

The same procedure as described in Example 6 above was followed up to 800°C, at which temperature the samples were held for 1 hour. Thereafter, heating of the
5   samples was resumed at the rate of 1°C/min to 1000°C, where the temperature was maintained for 0.5 hours. After cooling in argon, the samples were passivated using 3% O_2/Ar. XRD phase analysis indicated that the precursors have converted into β-Mo_2C.

RESULTS OF EXAMPLES 1-7

Carbide nanorods and carbide nanoparticles supported on carbon nanotubes were
10   prepared according to Examples 1 to 7 above. Table 1 below summarizes the experimental conditions and XRD results for selected experiments.

TABLE 1. SUMMARY OF RESULTS FOR MOLYBDENUM CARBIDE PREPARATIONS

SAMPLE	Mo Source	T°C	C:Mo initial	Weight loss (theor.)	PHASES, XRD
1	Moacac (s)[b]	600	4 (94)[e]	27 (44)	C, MoO_2, Mo_2C (hex)
2	MoO_3 (s)[a]	800	35 (38)[e]	23 (35)	C, Mo_2C (cub)
3	MoO_3 (s)[a]	800	40 (34)[e]	n/a	C, Mo_2C (hex)
4	Moacac (s)[b]	800	10 (85)[e]	31 (32)	C, Mo_2C (hex)
5	Moacac (s)[b]	800	20 (57)[e]	27 (22)	Mo_2C (hex/cub), Mo
6	MoO_3 (s)[b]	1000	10 (85)[e]	41 (32)	Mo_2C (hex), Mo
7	MoO_3 (s)[b]	1000	20 (57)[e]	27 (22)	Mo_2C (hex/cub), Mo
8	MoO_3 (s)[b]	1000	10 (85)[e]	38 (32)	C, Mo_2C (hex)
9	MoO_3 (s)[b]	625	30 (43)[e]	20 (17)	C, Mo_2C (hex/cub)
10	MoO_3 (s)[b]	625	20 (57)[e]	27 (22)	C, Mo_2C (hex), MoO_2
11	MoO_3 (s)[b]	1000	50 (28)[e]	12 (11)	C, Mo_2C (hex/cub)
12	MoO_3 (s)[c]	800	3.5 (100)[e]	55 (55)	Mo_2C (hex/cub)

[a] Impregnated powder of aggregates of carbon nanotubes
30   [b] Impregnated extrudates of aggregates of carbon nanotubes
[c] Powder of aggregates of carbon nanotubes physically mixed with Mo precursor
[e] Calculated Mo_2C loading in final calcined product assuming full conversion of Mo precursor to Mo_2C

The chemical reaction involved in the preparation of Samples 1-12 is:

$$2MoO_3 + 7C \rightarrow Mo_2C + 6\ CO.$$
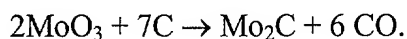
In the second column is a list of molybdenum precursors converted to Mo_2C by reaction with carbon nanotubes. Moacac refers to molybdenyl acetylacetonate, and MoO_3 refers to molybdenum trioxide. "(s)" refers to the solid phase of the molybdenum precursor. Superscripts a, b and c refer to methods of dispersing the reactants as described in Examples 2, 3 and 4, respectively. T°C refers to the final calcination temperature of the reaction temperature cycle. "C:Mo initial " refers to the atomic ratio of C:Mo in the original reaction mixture before conversion to a carbide compound. For example, the stoichiometric atomic ratio to produce pure carbide with no excess C or Mo, i.e., pure Mo_2C is 3.5. The number following in parentheses is the calculated loading of the Mo_2C contained in the resulting materials. "Weight loss (theor.)" refers to the theoretical weight loss according to the chemical equation. "Phases, XRD" shows the compounds found in the XRD analyses. Mo_2C exists in 2 distinct crystallographic phases, hexagonal and cubic.

Table 2 below summarizes the XRD results for the samples of Table 1.

TABLE 2. SUMMARY OF XRD RESULTS

Sample	Mo_2C (hex)	Mo_2C (cubic)	MoO_2
MoC	>100 nm		
1	15~20 nm		minor component
2		5~8 nm	
3		5~8 nm	
4	10~15 nm		
5	15~20 nm	~15 nm	
6	20 nm		
7	36~38 nm		
8	8~10 nm	8~10 nm	
9	18 nm		minor component
10	20~25 nm	5~8 nm	
11	35 nm		
12	26 nm		

Table 2 summarizes the XRD results for the experiments summarized in Table 1, identifies the compounds made, the phases present and the calculated average particle size for the different phases.

The average particle size is a volume-biased average size, such that the value of one large particle counts more heavily than several medium particles and much more than the volume of many small particles. This is a conventional procedure which is well known to those familiar with XRD methods.

5

Discussion of Results of Examples 1-7

A.   Unsupported Mo₂C Nanoparticles and Nanorods

Samples 1 and 12 provided the clearest evidence of the formation of free-standing Mo₂C nanorods and nanoparticles. These were obtained by reacting stoichiometric or near stoichiometric mixtures of MoO_3 and carbon nanotubes, either as powder or as

10   extrudates. Product identification and morphologies were obtained by SEM, HRTEM and XRD. In Example 1, with about 15% excess of carbon, the major product was identified by XRD as the hexagonal phase of Mo₂C. MoO_2 and graphitic carbon were seen as minor components. SEM showed the presence of both nanorods (approximately 10 to 15 nm in diameter) and nanoparticles (approximately 20 nm).

15   Samples 11 and 12 were obtained by reaction carbon nanotubes with either a stoichiometric mixture of well-dispersed MoO_3 powder or with impregnated ammonium molybdate. More evidence of the formation of Mo₂C nanorods and nanoparticles was obtained in Sample 12, obtained by reacting a stoichiometric mixture of MoO_3 and powder of carbon nanotubes. XRD, SEM and HRTEM analyses showed formation of

20   both Mo₂C nanorods and nanoparticles. The SEM analyses showed a network of nanorods with nanoparticles distributed within the network as shown in Figure 1. Accurate dimensions of carbide nanorods have been obtained by HRTEM as shown in Figure 2, which shows carbide nanorods having diameters similar to those of carbon nanotubes, namely, about 7 nm. The carbide nanoparticles particles ranged from about 7

25   nm to about 25 nm in diameter.

Sample 12, a stoichiometric mixture, was studied in more detail in order to learn the course of the reaction. The reaction was tracked by thermogravimetric analysis (TGA) as shown in Figure 4. Figure 4 shows that the stoichiometric reaction has occurred in two distinct steps, namely, reduction of MoO_3 by carbon to MoO_2 at from

about 450 to about 550 °C, followed by further reduction to Mo_2C at from about 675 °C

to about 725 °C. SEM and XRD analyses taken after calcination at 600°C showed a

complete redistribution of oxide precursor from the very large, supra-micron particles of

MoO_3 initially present to about 20 to 50 nm particles of MoO_{3-x}, well-dispersed amongst

5   individual fibrils. This redistribution probably occurred through vaporization. Further

calcination to 800° C converted the MoO_{3-x} (wherein x is 0 or 1) mixture to Mo_2C

nanorods and nanoparticles, with further reduction in particle size from about 7 to about

25 nm. Without being bound by any theory, even though redistribution of MoO_3

probably takes place through vaporization, both chemical transformations (MoO_3

10    $\rightarrow MoO_2$ and $MoO_2 \rightarrow Mo_2C$) by reduction by carbon are believed to occur through solid-

solid phase reactions.

B.   Mo₂C Nanoparticles Supported on Carbon Nanotubes

XRD, SEM and HRTEM analyses of products from Sample 10 provided evidence

for the successful preparation of nanoparticles of Mo_2C supported on individual carbon

15   nanotubes. These products were formed by impregnation of ammonium molybdate from

aqueous solution onto CC aggregates of carbon nanotubes and carefully calcined as

shown in Table 1. XRD's of both products showed the cubic form of Mo_2C to be the

major component along with graphitic carbon. Hexagonal Mo_2C was seen as a minor

component. No molybdenum oxide was detected. The cubic Mo_2C particles ranged

20   from about 2 to about 5 nm in diameter, while the hexagonal particles ranged from about

10 to about 25 nm. The cubic particles were mainly deposited on individual carbon

nanotubes, while the hexagonal particles were distributed between carbon nanotubes.

These can be seen in Figures 3 and 4, which are copies of HRTEM micrographs taken

from Sample 10. In these pictures, the particle size can be estimated by direct

25   comparison with the fibril diameters, which range from 7 to 10 nm.

EXAMPLE 8

Preparation of Tungsten Carbide Precursors by Impregnation with Ammonium Tungstate

The procedure used in Example 2 above was followed, except that the

impregnating solution was an aqueous solution containing the correct amount of

30   ammonium paratungstate hydrate ($(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ 72% W, referred to as

ammonium tungstate) necessary for the desired C:W atom ratio loading (C:W mole ratios of 3.5:1, 10:1 and 20:1). The resulting mixture was dried at 225°C in full vacuum for 18 hours during which the paratungstate compound was decomposed to WO_3. The sample was set aside for conversion to carbide catalysts by careful calcination under an inert

5 atmosphere as more particularly described in Example 10.

EXAMPLE 9

Preparation of Tungsten Carbide Precursors by Impregnation with Phosphotungstic Acid

The procedure used in Example 8 above was followed, except that the impregnating solution was an aqueous solution containing the correct amount of

10 phosphotungstic acid ($H_3 PO_4 \cdot 12 WO_3 \cdot xH_2O$, 76.6% W referred to as PTA), necessary for the desired C:W atom ratio loading (C:W mole ratios of 3.5:1, 10:1 and 20:1.) The resulting mixture was dried at 225°C in full vacuum for 18 hours during which the PTA was decomposed to WO_3. The sample was set aside for conversion to carbide catalysts by careful calcination under an inert atmosphere as more particularly described in

15 Example 10.

EXAMPLE 10

Calcination of Tungsten Carbide Precursors at 1000°C

The procedure described in Example 7 above was followed to convert precursors of tungsten carbides to tungsten carbides. After cooling in argon, the samples were

20 passivated using 3% O_2/Ar. Table 3 below summarizes the experimental conditions and XRD results for selected experiments.

TABLE 3. SUMMARY OF RESULTS FOR TUNGSTEN CARBIDE PREPARATIONS

SAMPLE	W Source	T° C	C:W INITIAL	PHASES, XRD
1	PTA and CC[a]	1000	3.5:1	WC and W_2C
2	PTA and CC	1000	10:1	WC and W_2C
3	PTA and CC	1000	20:1	WC and W_2C
4	A. Tung and CC[b]	1000	3.5:1	WC, W_2C and possibly W
5	A. Tung and CC	1000	10:1	WC and W_2C
6	A. Tung and CC	1000	20:1	WC and W_2C

[a] Impregnated powder of CC aggregates of carbon nanotubes by incipient wetness with phosphotungstic acid

[b] Impregnated powder of CC aggregates of carbon nanotubes by incipient wetness with ammonium paratungstate hydrate

The chemical reactions involved in the preparation of Samples 1-6 summarized in table 3 are:

$$WO_3(s) + 4C \rightarrow WC + 3\ CO \text{ and } 2WO_3(s) + 7C \rightarrow W_2C + 6\ CO.$$
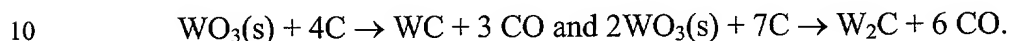
In the second column of Table 3 is a list of tungsten precursors which were converted to W_2C/WC by reacting with carbon nanotubes. PTA refers to phosphotungstic acid and A. Tung refers to ammonium paratungstate hydrate. "(s)" refers to the solid phase of the tungsten precursor. C:W refers to the ratio of C atoms to W atoms in the original mix. The stoichiometric atom ratio to produce pure WC with no excess of C or W is 4.0. To produce pure W_2C, the atom ratio C:W is 3.5. The XRD column lists the compounds observed in the XRD analyses.

EXAMPLES 11-13

Preparation of a Catalyst Support of Extrudates of Silicon Carbide Nanorods

SiC nanorods were prepared from Hyperion aggregates of carbon nanotubes in accordance with Example 1 of U.S. Application Serial No. 08/414,369 filed March 31, 1995 by reacting the carbon nanotubes with ISO vapor at high temperature. The resulting SiC nanorods have a uniform diameter of fifteen nm on average and a highly crystallized β-SiC structure.

Poly(dimethylsiloxane) as provided by Aldrich Chemicals of Milwaukee, Wisconsin was used as a binder for the preparation of extrudates of SiC nanorods. 0.16g of SiC nanorods and 0.16g of poly(dimethylsiloxane) were mixed to form a uniform thick paste. Subsequently, the paste was pushed through a syringe to produce extrudates

having a green color which were heated under flowing argon atmosphere under the following conditions: at 200°C for 2 hours (Example 11); at 400°C for 4 hours (Example 12); and at 700°C for 4 hours (Example 13). A rigid porous structure of SiC nanorods was formed.

5   The extrudates obtained in Examples 11-13 had a density of 0.97 gm/cc and a bimodal pore structure. The macropores were 1 to 5 μm, as shown in Fig. 5B among aggregates and the mesopores were 10 to 50 nm, as shown in Figure 5C in the networks of intertwined SiC nanorods. The diameter of the extrudates was about 1.2 nm as shown in Figure 5A. The specific surface area of the extrudates of SiC nanorods was 97 m^2/gm.

10   Because of their high surface area, unique pore structure and high temperature stability, the SiC extrudates are attractive for various applications, including as supports for catalysts such as platinum, palladium other catalytic metals and carbides of Mo, W, V, Nb or Ta. The surface properties of SiC nanorods when used as a catalyst support are very close to those of carbon. Conventional carbon supports can therefore be replaced

15   with SiC extrudates. Many properties of carbon supported catalysts can be realized in high temperature conditions, as required, in particular, for oxidation reactions.

EXAMPLES 14 AND 15
Preparation by Reductive Carburization of Extrudates of Carbon Nanotubes
Including Molybdenum Carbides

20   Two samples of 5 gms of extrudates of carbon nanotubes having a volatile molybdenum compound on the surface thereof prepared according to Example 14 are charged into alumina boats. Each boat is placed into a tube furnace and heated under flowing argon for 2 hours at 250°C and 450°C, respectively. The gas is changed from argon to a mixture of CH_4/H_2 (20% CH_4) and the furnace is slowly (1°C/min) heated up

25   to 650°C where the temperature is maintained for 1 hour. Molybdenum carbides supported on the surface of the extrudates of the carbon nanotubes are obtained.

EXAMPLE 16
Preparation by Reactive Chemical Transport
of Extrudate of Molybdenum Carbide Nanorods

30   One gram of an extrudate of carbon nanotubes, 8 gms of molybdenum powder and 50 mg of bromine contained in a glass capsule are placed into a quartz tube which is

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evacuated at 10^{-3} Torr and then sealed. After the bromine capsule is broken, the tube is placed into a tube furnace and heated at 1000°C for about 1 week. The extrudates of carbon nanotubes are substantially converted to molybdenum carbide nanorods.

EXAMPLE 17

5

Preparation by Carburization of Molybdenum Carbides Supported on the Surface of Extrudates of Carbon Nanotubes

A sample of an extrudate of carbon nanotubes is placed in a vertical reactor such that a bed is formed. The extrudate is heated under flowing H_2 gas at 150°C for 2 hours. Thereafter, the extrudate is cooled to 50°C. H_2 gas passed through a saturator containing

10    $Mo(CO)_6$ at 50°C is passed over the cooled extrudates of carbon nanotubes. As a result, $Mo(CO)_6$ becomes adsorbed on the surface of the extrudate. Following the adsorption of $Mo(CO)_6$, the temperature of the sample is raised to 150°C in an atmosphere of pure H_2. The temperature is maintained at 150°C for 1 hour. The temperature of the sample is then increased at 650°C and maintained at this temperature for 2 hours under flowing H_2

15   gas. A sample of the extrudate of carbon having molybdenum on its surfaces is obtained. This sample is kept at 650°C for 1 hour. The gas is switched from H_2 to a CH_4/H_2 mixture (20% CH_4). The molybdenum adsorbed on the surfaces of the carbon nanotubes is converted to molybdenum carbide. The amount of molybdenum carbide formed on the surface of the extrudate can be controlled, by varying the duration of adsorption of the

20    $Mo(CO)_6$ over the cooled carbon nanotube extrudate.

EXAMPLE 18

Use of Mo_2C Nanoparticles and/or Nanorods Supported on Aggregates of Carbon Nanotubes in the Vapor Phase Hydrogenation of Ethylene

A vapor phase reactor was assembled by inserting a 6 mm quartz thermowell

25   upward through the bottom end of a vertical quartz tube having an outer diameter of 12 mm. A porous plug of quartz wool was placed at the tip of the thermowell to support a bed of catalyst powder. One gram of the catalyst of Sample No. 2 in Table 1 was crushed and sieved to (+80-60) standard mesh and placed onto the quartz wool plug. The tube was placed vertically into a ½ inch tube furnace as described in Example 6. The top of

30   the tube was fitted with gas inlet lines to feed reactant gases, and the bottom of the tube was fitted with an exit line connected to a 0-15 psi pressure gauge. Rotometers in the gas

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inlet lines controlled the flows and thus the ratios of the individual reactant gases. Product gases were fed through a gas sampling valve to a Varian gas chromatograph equipped with a GS-Q capillary column suitable for analyzing C_1-C_5 alkanes and olefins.

Ethylene and hydrogen gases were fed to the vapor phase reactor described in molar ratios ranging from 1:1 to 4:1 ethylene:H_2 at 70°C initial temperature, 1-3 psi gauge total pressure at a gas space velocity (GSV) 60-325 min^{-1}. In each run, the temperature of the catalyst bed was held at the set temperature of 70°C for several minutes, and then rapidly increased to approximately 200°C in several minutes. The temperature of the catalyst bed remained relatively constant thereafter. Analyses by gas chromatography showed 100% conversion of ethylene to ethane. Ethane was the only product observed, i.e., the selectivities of the reaction approached 100%.

EXAMPLE 19

Preparation of Oxycarbide Containing Nanorods Catalyst In Situ and Use of in the Vapor Phase Isomerization of Butane to Isobutane

The catalyst Sample 12 of Table 1 was oxidized to form oxycarbide nanorods. This unsupported catalyst was then used to isomerize butane to isobutane. A 1.0 gram sample of ground catalyst (+80-60) was placed in a reactor as described in Example 18. The catalyst was treated with 10% H_2 in argon at 700°C for 30 minutes, cooled in argon to room temperature, and then treated with 3% O_2 in argon at 350°C for 14 hours to obtain oxycarbide-containing nanorods. After purging the system of O_2, mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure were fed to the reactor at a WHSV 1 hr^{-1} to 10 hr^{-1}. The products were analyzed by GC using a GS-Q capillary column.

A steady yield of 4.4% isobutane was obtained at 380°C at a WHSV 10 hr^{-1}. Conversion of n-butane was approximately 4.5% with selectivity to isobutane of about 96% based on GC analyses. The byproducts, in order of abundance, were propane, ethane and methane. Increasing the temperature to 420°C increased the conversion of n-butane to more than 10% isobutane. However, the selectivity to isobutane was less than 50%, with the major selectivity loss to methane.

EXAMPLE 20

Use of Mo$_2$C Nanoparticles and/or Nanorods Supported on Extrudates of
Aggregates of Carbon Nanotubes in the Vapor Phase Hydrogenation of Ethylene

A vapor phase reactor is assembled as described in Example 18. One gram of the catalyst Sample No. 9 in Table 1 is crushed and sieved to (+80-60) standard mesh and placed onto the quartz wool plug. The tube is placed vertically into a ½ inch tube furnace as described in Example 5. The top of the tube is fitted with gas inlet lines to feed reactant gases and the bottom of the tube is fitted with an exit line connected to a 0-15 psi pressure gauge. Rotometers in the gas inlet lines control the flows and thus the ratios of the individual reactant gases. Product gases are fed through a gas sampling valve to a Varian gas chromatograph equipped with a GS-Q capillary column.

Ethylene and hydrogen gases are fed to the vapor phase reactor in molar ratios ranging from 1:1 to 4:1 ethylene: H$_2$ at 70°C initial temperature, 1-3 psi gauge total pressure at a GSV 60-325 min^{-1}. In each run, the temperature of the catalyst bed is held at the set temperature of 70°C for several minutes, then rapidly increased to approximately 200°C in several minutes. The temperature of the catalyst bed remains relatively constant thereafter. Analyses by GC shows 100% conversion of ethylene to ethane. Ethane is the only product observed, i.e., selectivities approaching 100%.

EXAMPLE 21

Use of Mo$_2$C Nanoparticles and/or Nanorods Supported on Extrudates of Aggregates
of Carbon Nanotubes in the Vapor Phase Isomerization of Butane to Isobutane

The catalyst of Sample 11 of Table 1 was oxidized to form oxycarbide nanorods which were used to isomerize butane to isobutane. A 1.0 gram sample of ground catalyst (+80-60) was placed in a reactor as described in Example 18. In the reactor, the catalyst was then treated with 10% H$_2$ in argon at 700°C for 30 minutes, cooled in argon to room temperature, and then treated with 3% O$_2$ in argon at 350°C for 14 hours to obtain oxycarbide nanorods. After purging the system of O$_2$, mixtures of n-butane and H$_2$ in molar ratios of n-butane: H$_2$ ranging from 1:16 to 1:4 at 1-3 psi gauge pressure were fed to the reactor at WHSVs ranging from 1 to 10 hr^{-1}. The products were analyzed by GC using a GS-Q capillary column provided by J&W of Alltech Associates.

A steady yield of 4.4% isobutane was obtained at 380°C at a WHSV 10 hr^{-1}. Conversion of n-butane was approximately 4.5% with selectivity to isobutane of about 96% based on GC analyses. The byproducts, in order of abundance, were propane, ethane and methane. Increasing temperature to 420°C increased conversion of n-butane to more than 10%. The selectivity to isobutane was less than 50%, with the major selectivity loss to methane.

EXAMPLE 22

Use of Mo$_2$C Nanoparticles and/or Nanorods Supported on Aggregates of Carbon Nanotubes in the Hydrodesulfurization of Thiophene

0.1 gm of the catalyst of Sample 2 in Table 1 is charged into a 500 cc stirred autoclave with 300 cc of 1 vol% solution of thiophene in hexadecane. The reactor is charged to 80 atm with H$_2$ and the hydrodesulfurization reaction is carried out at 300° C. One cc samples are withdrawn and analyzed at 5-minute intervals and a pseudo first order rate constant for disappearance of thiophene is determined to be 4.5x10^{-3} L/gm cat-s.

EXAMPLE 23

Use of Unsupported Oxycarbide Nanorods as Catalyst in the Hydrodesulfurization of Thiophene

0.1 gm of catalyst described in Example 19 above is charged into a 500 cc stirred autoclave with 300 cc of 1 vol% solution of thiophene in hexadecane. The reactor is charged to 80 atm with H$_2$ and the hydrodesulfurization reaction is carried out at 300° C. One cc samples are withdrawn and analyzed at 5 minute intervals and a pseudo first order rate constant for disappearance of thiophene is determined to be 4.5x10^{-3} L/gm cat-s.

EXAMPLE 24

Use of WC/W$_2$C Nanoparticles and/or Nanorods Supported on Aggregates of Carbon Nanotubes in the Vapor Phase Hydrogenation of Ethylene

A vapor phase reactor is assembled as described in Example 18. One gram of the catalyst of Sample 1 in Table 3 is crushed and sieved to (+80-60) standard mesh and placed onto the quartz wool plug. The tube is placed vertically into a ½ inch tube furnace as described in Example 10. The top of the tube is fitted with gas inlet lines to feed reactant gases, and the bottom of the tube is fitted with an exit line connected to a 0-15 psi pressure gauge. Rotometers in the gas inlet lines control the flows and thus the ratios

of the individual reactant gases. Product gases are fed through a gas sampling valve to a Varian gas chromatograph equipped with a GS-Q capillary column suitable for analyzing C_1-C_5 alkanes and olefins.

Ethylene and hydrogen gases are fed to the vapor phase reactor in molar ratios ranging from 1:1 to 4:1 ethylene: H_2 at 70°C initial temperature, 1-3 psi gauge total pressure and at WHSVs of 65-325 min^{-1}. In each run, the temperature of the catalyst bed is held at the set temperature of 70°C for several minutes, then it is rapidly increased to approximately 200°C in several minutes. The temperature of the catalyst bed remains relatively constant thereafter. Analyses by GC shows 100% conversion of ethylene to ethane. Ethane is the only product observed, i.e., the selectivities approach 100%.

EXAMPLE 25

Preparation of Tungsten Oxycarbide Nanorods Catalyst In Situ and Use of Same in the Vapor Phase Isomerization of Butane to Isobutane

The catalyst of Sample 2 of Table 3 is oxidized to form unsupported oxycarbide nanorods which are used to isomerize butane to isobutane. A 1-gram sample of ground catalyst (+80-60) is placed in a reactor as described in Example 24. In the reactor, the catalyst is treated with 10% H_2 in argon at 700°C for 30 minutes, cooled in argon to room temperature, and then treated with 3% O_2 in argon at 350°C for 14 hours to obtain tungsten oxycarbide containing nanorods. After purging the system of O_2, mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are fed to the reactor at WHSVs of 1 to 10 hr^{-1}. The products are analyzed by GC using a GS-Q capillary column as provided by Alltech Associates.

A steady yield of 4.4% isobutane is obtained at 380°C and at a WHSV of 1 to 10 hr^{-1}. Conversion of n-butane is approximately 4.5% with selectivity to isobutane of about 96% based on GC analyses. The byproducts, in order of abundance, are propane, ethane and methane. Increasing temperature to 420°C increases conversion of n-butane to more than 10% isobutane. The selectivity to isobutane is less than 50% with the major selectivity loss to methane.

EXAMPLE 26

Use of WC/W₂C Nanoparticles and/or Nanorods Supported on Aggregates of Carbon Nanotubes in the Hydrodesulfurization of Thiophene

0.1 gram of the catalyst of Sample 1 in Table 3 is charged into a 500 cc stirred autoclave with 300 cc of 1 vol% solution of thiophene in hexadecane. The reactor is charged to 80 atm with H_2 and the hydrodesulfurization reaction is carried out at 300° C. One cc samples are withdrawn and analyzed at 5-minute intervals and a pseudo first order rate constant for disappearance of thiophene is determined to be 4.5×10^{-3} L/gm cat-s.

EXAMPLE 27

Use of Unsupported Tungsten Oxycarbide Nanorods as Catalyst in the Hydrodesulfurization of Thiophene

0.1 gram of the catalyst in Example 25 is charged into a 500 cc stirred autoclave with 300 cc of 1 vol% solution of thiophene in hexadecane. The reactor is charged to 80 atm with H_2, and the hydrodesulfurization reaction is carried out at 300° C. One cc samples are withdrawn and analyzed at 5-minute intervals and a pseudo first order rate constant for disappearance of thiophene is determined to be 4.5×10^{-3} L/gm cat-s.

EXAMPLE 28

Preparation of a Pd Catalyst Supported on SiC Extrudates.

A 5 weight% Pd/SiC extrudate catalyst is prepared by contacting 10.0 gm SiC extrudates prepared in Example 12 with a solution containing 1.455 gms Pd(acetylacetonate)₂ (34.7% Pd, obtained from Alfa/Aesar of Ward Hill, Massachusetts) dissolved in 500 cc toluene. The mixture is stirred lightly for 1 hour, after which the toluene is removed at reduced pressure and 40°C in a rotary evaporator. The resulting dark brown solids are dried at 80°C overnight, then calcined at 350°C in air for 16 hours.

EXAMPLE 29

Preparation of a Pt catalyst supported on SiC extrudates.

A 1 weight % Pt/SiC extrudate catalyst is prepared by contacting 10.0 gms SiC extrudates prepared in Example 12 with a 6 N HCl solution containing 0.174 gram PtCl₄ (58% Pt, obtained from Alfa/Aesar). The mixture is stirred lightly for 1 hour after which

solvent is removed at reduced pressure and 70°C in a rotary evaporator. The resulting brown solids are dried at 140°C.

EXAMPLE 30

Oxidation of CH_4 with the Pd/SiC Extrudate Catalyst Prepared in Example 28.

5   Five gms of catalyst prepared in Example 28 are packed into a vertical ½" stainless steel tubular reactor to a height of about 2½". A wad of quartz wool placed atop a ¼" stainless steel thermowell inserted upward from the bottom of the tube supports the catalyst bed. The inlet and outlet of the tube reactor are fitted to allow passage of gas into the reactor, through the catalyst bed and out of the reactor. The effluent gas is

10   analyzed by a gas chromatograph using a Poropak Q column manufactured by Millipore Corp. of Bedford, Massachusetts, which allows quantitative analysis of CH_4, CO and CO_2. Temperature of the reactor is measured by a thermocouple inserted in the thermowell. The reactor is then placed in a 1" Lindberg furnace to provide heat.

The catalyst is reduced *in situ* with 5 % H_2/N_2 at 350°C for 12 hours. After

15   purging residual H_2 with N_2, at atmospheric pressure, a gas mixture comprising 4% $O_2/1\%$ $CH_4/95\%$ N_2 is passed over the catalyst bed at 450°C at a total gas rate of 50 l (stp)/hr. Gas chromatograph analysis shows a conversion of $CH_4 > 99$ mole% at about 100% selectivity to CO_2.

EXAMPLE 31

Oxidation of CO with the Pt/SiC Extrudate Catalyst Prepared in Example 29.

20

The reactor used in Example 30 is loaded with 5 gms of catalyst. The catalyst is reduced *in situ* with 5% H_2/N_2 for 2 hours at 350°C, after which the reactor is purged of H_2 by N_2. At atmospheric pressure, a gas mixture comprising 5% $O_2/1\%$ CO and 94% argon is passed over the catalyst at 300°C at a total gas rate of 40 l (stp)/hr. Gas

25   chromatographic analyses show complete conversion of CO to CO_2.

EXAMPLES OF MAKING ACIDIFIED CARBIDES AND/OR OXYCARBIDES

EXAMPLE 32

Halogen Treatment of Oxygenated Molybdenum Carbide

Two gms samples from Examples 5, 6 or 7 are placed in a 1-inch micro-reactor.

5   First the reactor temperature is raised to 600°C under flow of argon to dry the sample.

The carrier gas is then switched to 5% Cl$_2$/Ar and the chlorination is allowed to proceed

at 300°C for 1 hour. Upon completion, the sample is cooled down and purged with argon

for 30 minutes and stored under argon.

EXAMPLE 33

10   Carbon Tetrachloride Treatment of Oxygenated Molybdenum Carbide

Two gms samples from Examples 5, 6 or 7 are placed in a 1-inch micro-reactor.

First the reactor temperature is raised to 600°C under flow of argon to dry the sample.

The carrier gas is then passed through a gas-liquid saturator containing pure CCl$_4$. The

temperature of the saturator is kept at 0°C in an ice-water bath. Chlorination is allowed

15   to proceed at 300°C for 1 hour. Upon completion, the sample is cooled down and purged

with argon for 30 minutes and stored under argon.

EXAMPLE 34

Halogen Treatment of Hydrogen Pretreated Molybdenum Carbide

Two gms samples prepared using the procedure described in Examples 5, 6 or 7

20   are placed in a 1-inch micro-reactor and heated in hydrogen at temperatures up to 500°C.

After 30 minutes of treatment, the reactor is cooled to 200°C and purged with argon. The

carrier gas is then switched to 5% Cl$_2$/Ar and the chlorination is allowed to proceed at

200°C for 2 hours. Upon completion, the sample is cooled down and purged with argon

for 30 minutes and stored under argon.

EXAMPLE 35

25

Carbon Tetrachloride Treatment of Hydrogen Pretreated Molybdenum Carbide

Two gms samples prepared using the procedure described in Examples 5, 6 or 7

are placed in a 1-inch micro-reactor and heated in hydrogen at temperatures up to 500°C.

After 30 minutes of treatment, the reactor is cooled to 200°C and purged with argon. The

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carrier gas is then passed through a gas-liquid saturator containing pure CCl_4. The temperature of the saturator is kept at 0°C in an ice-water bath. Chlorination is allowed to proceed at 200°C for 2 hours. Upon completion, the sample is cooled down and purged with argon for 30 minutes and stored under argon.

5

EXAMPLE 36

Acidifying Mo Carbide Surface with Ammonia

Two gms samples prepared using the procedure described in Examples 5, 6 or 7 were placed in a 1-inch micro-reactor. The acidification was carried out by reacting the samples with NH_3 at temperatures up to 700°C. After the reaction, the samples were held

10   at 700°C for 1 hour, the reactor was then purged with N_2 and cooled down to room temperature. The treated sample was then stored under N_2.

EXAMPLE 37

Acidifying Mo Carbide Surface with Phosphate

Ammonium phosphate $((NH_4)H_2PO_4)$ was added to nanotubes by incipient

15   wetness impregnation. The loading was typically in the range of 0.2 - 5 mol%. The impregnated sample was then dried and calcined in air at 300°C for 2 hours. The modified fibrils were designated as PF.

A procedure similar to that used in Example 2 above followed except the powdery samples of CC aggregates were replaced by PF. The calcined samples having the desired

20   C:Mo ratio were set aside for conversion to carbide catalysts by careful calcination under an inert atmosphere as described in Examples 6 or 7. Post-synthesis XPS analysis indicated that phosphorus was strongly bonded to Mo atoms.

EXAMPLE 38

Incorporation of $AlCl_3$ onto Molybdenum Carbide Nanorods/Nanoparticles

25   Molybdenum carbide nanorods or nanoparticles are prepared following the procedures described in Examples 1-7. The C:Mo atomic ratio is controlled at 5 or lower to obtain a pure or highly concentrated molybdenum carbide phase. Both XRD and SEM confirm the formation of β-Mo_2C - containing nanorods or nanoparticles. The prepared samples are transferred into a three-neck flask under an argon blanket. An ethanol

solution of $AlCl_3$ is then added using the incipient wetness method amount. The resulting mixture is dried at 110°C under argon and then calcined at 200°C for 1 hour.

EXAMPLE 39

Incorporation of Chlorinated Alumina on Mo Carbide Containing Aggregates by Co-Impregnation of $Al(NO_3)_3 \cdot 9H_2O$ and $(NH_4)6Mo7O24$ Followed by Chlorination

As grown CC or CY nanotube aggregates were oxidized with nitric acid as described in Example 3 to form oxidized CC aggregates having an acid titer of about 0.6 meq/gm.

Five gms oxidized CC aggregates are impregnated by incipient wetness with aqueous solutions containing the amount of ammonium heptamolybdate tetrahydrate and aluminum nitrate necessary for the desired C:Mo:Al atomic ratio. The resulting mixtures are dried at 225°C in full vacuum for 18 hours during which time the heptamolybdate and the aluminum nitrate are decomposed to MoO_3 and Al_2O_3.

Weighed samples of molybdenum carbide-alumina precursors are loaded into porcelain boats that were then placed horizontally in a 1-inch quartz tube. The procedure described in Example 7 is followed at temperatures up to 1000°C. XRD phase analysis indicates that the final form of Mo and Al compounds are β-Mo_2C and Al_2O_3. After cooling down to room temperature under argon, the carrier gas is passed through a gas-liquid saturator containing pure CCl_4. The temperature of the saturator is kept at 0°C in an ice-water bath. Chlorination is allowed to proceed at 200°C for 2 hours. Upon completion, the sample is cooled down and purged with argon for 30 minutes and stored under argon.

EXAMPLE 40

Incorporation of Zirconia in Molybdenum Carbide Catalyst

As grown CC or CY nanotube aggregates were oxidized with nitric acid as described in Example 3 to form oxidized CC aggregates having an acid titer of about 0.6 meq/gm.

Five gms oxidized CC type aggregates are impregnated by incipient wetness with aqueous solutions containing the amount of ammonium heptamolybdate tetrahydrate and

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zirconium dinitrate oxide ($ZrO(NO_3)_2 \cdot xH_2O$) necessary for the desired C:Mo:Zr atomic ratio. The resulting mixtures are dried at 225°C in full vacuum for 18 hours during which the heptamolybdate and the aluminum nitrate are decomposed to MoO_3 and ZrO_2.

The solids are then placed horizontally in a 1-inch quartz tube. The procedure in
5   Example 5 is followed at temperatures up to 900°C.

EXAMPLES SHOWING REACTIONS CONDUCTED
USING THE CATALYSTS OF THE INVENTION
EXAMPLE 41

10   Preparation of Oxycarbide Nanorods Catalyst *In Situ* and Use of Same
in the Vapor Phase Isomerization of n-Butane to Isobutane

A molybdenum carbide nanorod catalyst was prepared using the procedure described in Example 2 with C:Mo=3.5 followed by a calcination procedure described in Example 6. This catalyst was oxidized to form unsupported oxycarbide nanorods which
15   were used to isomerize n-butane to isobutane.

A vapor phase reactor as described in Example 18 was assembled. One gram of ground catalyst, approximately 60 to 80 mesh, was placed onto the quartz wool plug. In the reactor, the catalyst was treated with 10% hydrogen in argon at 700°C for 30 minutes, cooled in argon to room temperature, and then treated with 3% oxygen in argon at 350°C
20   for 14 hours to obtain oxycarbide nanorods. After purging the system of oxygen, mixtures of n-butane and hydrogen in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure were fed to the reactor at WHSVs of 1-10 h^{-1}. A steady yield of 4.4% isobutane was obtained at 380°C at a WHSV of 10 h^{-1}. Conversion of n-butane was approximately 4.5% with selectivity to isobutane of about 96% based on GC
25   analyses. The byproducts, in order of abundance, were propane, ethane and methane. Increasing the temperature to 420°C increased conversion of n-butane to more than 10% at selectivities to isobutane less than 50%. The major selectivity loss to methane.

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EXAMPLE 42

n-Butane Isomerization with Chlorine-treated Molybdenum Carbide Catalyst

One gram of the catalyst in Example 32 is placed in the micro-reactor described above in Example 18. Mixtures of n-butane and H_2 in molar ratios of n-butane:H_2

5 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are passed through a liquid saturator containing pure CCl_4 held at -20°C and fed to the reactor at WHSVs of 1-10 h^{-1}. At 300°C, a steady butane conversion of about 20% is achieved with selectivity to isobutane of more than 96%.

EXAMPLE 43

10 ### n-Butane Isomerization with $AlCl_3$/Molybdenum Carbide Catalyst

One gram of the catalyst of Example 38 is placed in the micro-reactor described in Example 18. Mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are passed through a liquid saturator containing pure CCl_4 held at -20°C and fed to the reactor at WHSVs of 1-10 h^{-1}. At 300°C, a steady

15 butane conversion of about 50% is achieved with selectivity to isobutane of more than 96%.

EXAMPLE 44

n-Butane Isomerization with Chlorinated Molybdenum Carbide-Alumina Catalyst

One gram of the catalyst of Example 14 is placed in the micro-reactor described

20 in Example 18. Mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are passed through a liquid saturator containing pure CCl_4 held at -20°C and fed to the reactor at WHSVs of 1-10 h^{-1}. At 300°C, a steady butane conversion of about 50% is achieved with selectivity to isobutane of more than 96%.

25 ## EXAMPLE 45

n-Butane Isomerization with Treated with Ammonia Molybdenum Carbide Catalyst

One gram of the catalyst of Example 36 is placed in the micro-reactor described in Example 18. Mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are fed to the reactor at WHSVs of 1-10 h^{-1}. At

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300°C, a steady butane conversion of about 10% is achieved with selectivity to isobutane of more than 96%.

EXAMPLE 46

n-Butane Isomerization with Phosphorus-Incorporated Molybdenum Carbide Catalyst

One gram the catalyst of Example 37 is placed in the micro-reactor in Example 18. Mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are fed to the reactor at WHSVs of 1-10 h^{-1}. At 300°C, a steady butane conversion of about 10% is achieved with selectivity to isobutane of more than 96%.

EXAMPLE 47

n-Butane Isomerization with Molybdated Zirconia/Molybdenum Carbide Catalyst

One gram of the catalyst made from Example 40 is placed in the micro-reactor described in Example 18. The catalyst is first treated with 3% O_2 in argon at 350°C for 12 hours to obtain molybdated zirconia. After purging the system of O_2, mixtures of n-butane and H_2 in molar ratios of n-butane:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are fed to the reactor at WHSVs of 1-10 h^{-1}. At 350°C, a steady butane conversion of about 10% is achieved with selectivity to isobutane of more than 96%.

Table 4 summarizes the results obtained in Examples 41 to 47.

TABLE 4. SUMMARY OF RESULTS FOR ISOMERIZATION OF n-BUTANE TO ISOBUTANE

SAMPLE	CATALYST	T° C	n-BUTANE CONVERSION	ISOBUTANE SELECTIVITY
41	Unsupported Oxycarbide Nanorods	380	4.5%	96%
41	Unsupported Oxycarbide Nanorods	420	10%	< 50%
42	Cl Treated Mo_2C	300	20%	> 96%
43	$AlCl_3$/Mo_2C	300	50%	> 96%
44	Cl Mo_2C-Alumina	300	50%	> 96%
45	Treated with Ammonia Mo_2C	300	10%	> 96%
46	P Incorporated Mo_2C	300	10%	> 96%
47	Molybdated Zirconia/Mo_2C	350	10%	> 96%

As shown in Table 4, the untreated catalysts achieve conversions between 4.5% and 10% and selectivities to isobutane of from < 50% to 96%. In contrast, the acidified catalytic compositions achieve conversions greater than 10% and selectivities to isobutane of greater than 96%. The reactions using the acidified catalytic compositions are also run at lower temperatures than reactions using untreated catalysts.

EXAMPLE 48

1-Butene Isomerization with Chlorinated Molybdenum Carbide-Alumina Catalyst

One gram the catalyst of Example 14 is placed in the micro-reactor as described in Example 18. Mixtures of 1-butene and H_2 in molar ratios of 1-butene:H_2 ranging from 1:16 to 1:4 at 1-3 psi gauge pressure are fed to the reactor at WHSVs of 1-10 h^{-1}. At 80°C, a steady 1-butene conversion of about 30% is achieved with selectivity to 2-butene of more than 96%.

The terms and expressions which have been employed are used as terms of description and not of limitations, and there is no intention in the use of such terms or expressions of excluding any equivalents of the features shown and described as portions thereof, it being recognized that various modifications are possible within the scope of the invention.

Thus, while there had been described what are presently believed to be the preferred embodiments of the present invention, those skilled in the art will appreciate that other and further modifications can be made without departing from the true scope of the invention, and it is intended to include all such modifications and changes as come within the scope of the claims.